THE GEOCHEMISTRY OF FJORDS OF SOUTH-WEST NORWAY

by

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Frontispiece: View westwards along Bolstadfjord from the mouth of the River Vosso (seen as a marked surface outflow at left, centre of the photograph). The waters just visible beyond the precipitous cliff at the fjord's southern side lie within the inner basin of Bolstadfjord. This basin has a maximum depth of 80m and its waters are anoxic below 55m.

ABSTRACT

The fjords studied comprise part of a larger system of marine basins, each having a relatively shallow threshold at its mouth. A more or less normal estuarine circulation exists in the near-surface waters of all the fjords, but their deep water characteristics differ considerably. In Osterfjord the boundary between oxic and anoxic conditions occurs within the sediment; in Mofjord, Molviksfjord and the middle basin of Bolstadfjord, it coincides with the sediment-water interface; within the inner basin of Bolstadfjord, it occurs in the water column some 30m above the sediment surface. There is a build-up of dissolved phosphate-P, silicate-Si and titration alkalinity far in excess of their normal sea water concentrations within the anoxic waters of the inner basin of Bolstadfjord. This, together with an invariable decrease in dissolved oxygen content with depth in all the fjords, is due to decomposition of organic matter and a restricted circulation in the fjords' deeper waters.

The distribution of suspended particulate matter in the fjords is related to circulation, in situ biological productivity and physico-chemical processes. Surface waters (above the pycnocline) generally have higher detrital particulate matter contents than do intermediate waters. A maximum of detrital particulate matter often coincides with the pycnocline largely because the latter acts as a barrier to settling. In Osterfjord a high concentration of particulate matter in the bottom waters is due to resuspension of underlying sediment, whereas in the more restricted bottom waters of the other fjords there is no resuspension. The highest concentrations of in situ produced biogenic matter occur in the surface waters but do not always coincide with the pycnocline. Over half the particulate matter always comprises biogenous material. The major inorganic constituents are well-crystallised 10Å micaceous material and to a varying degree quartz and solid phases of Fe and Mn. While particulate K, Mg, Al and Ti are predominantly associated with detrital silicates, particulate Si and

Ca are additionally held in diatoms and skeletal carbonate respectively. Particulate P and S probably exist, at least in the surface waters, largely as biogenic matter. Compared to the underlying sediments, the suspended particulate matter is enriched in micaceous and biogenous material relative to quartz and feldspar.

The distributions of Mn and Fe are related to the position of the O_2-H_2S boundary irrespective of where it occurs relative to the sediment-water interface. They have been interpreted using models based on vertical diffusion-advection processes and redox reactions. Fe is incorporated into all the anoxic sediments as sulphide, while Mn is present in those occurring within the two outer basins of Bolstadfjord as a Mn(II) carbonate. Mn and probably Fe occur within the upper 1cm of sediment (oxic) from the deeper parts of Osterfjord as oxides-hydroxides.

In addition to the presence of Fe, Mn and S in authigenic phases and elements mainly associated with the lithogenous fraction of the sediments, Si occurs as diatoms; Ca, CO_2 and Sr as calcareous skeletal material, largely bivalves; and P as organic matter. The only elements, of 22 determined, whose contents consistently differ between oxic and anoxic sediments are organic C, S and Mo; all are enriched in the anoxic sediments. There are marked surface enrichments of Zn, Pb and sometimes Cu in all (anoxic and oxic) but one sediment core (19 examined). Two alternative explanations are given for this feature: they are a natural recycling process, which involves the release of bound metals during organic matter decomposition in the surface sediments (~0-10cm), and/or heavy metal pollution.

C O N T E N T S

TEXT

		Page
1.	INTRODUCTION	1
2.	INTRODUCTION TO THE AREA OF STUDY	
2.1	General	5
2.2	Geology and Sediment Supply to the Fjords	5
2.3	Geomorphology and Bathymetry of the Fjords	6
3.	HYDROGRAPHY	
3.1	Introduction	9
3.2	Salinity and Temperature	9
3.3	Dissolved Oxygen	11
3.4	Osterfjord	12
3.5	Molviksfjord	13
3.6	Mofjord	14
3.7	Bolstadfjord	16
3.8	Cause of Anoxicity	23
4.	HYDROCHEMISTRY	
4.1	Dissolved O_2, H_2S, Phosphate-P, Silicate-Si, and Titration Alkalinity within the Inner Basin of Bolstadfjord	25
4.2	Eh	29
4.3	pH	30
5.	SUSPENDED PARTICULATE MATTER	
5.1	Introduction	31
5.2	Major Constituents	32
5.3	Distribution of Suspended Particulate Matter	33
5.4	Elements Predominantly Associated with Detrital Silicates	35
5.5	Elements Predominantly Associated with Biogenous Material	39

Page

6. THE SEDIMENTS

6.1 Introduction 44

6.2 Description of the Sediments 45

6.3 Mineralogy 47

6.4 Major Element Geochemistry 48

a) Elements dominantly associated with the lithogenous fraction of the sediments 48

b) Calcium and CO_2 50

c) Iron and manganese 51

d) Sulphur, phosphorus, and organic C 53

6.5 Trace Element Geochemistry 56

a) Elements dominantly associated with the lithogenous fraction of the sediments 57
Rb 57
Zr 57
Y and Nb 58
Ni 58

b) Elements that are significantly associated with non-lithogenous constituents of the sediments 59
Sr 59
Zn, Pb and Cu 59
Mo 63

6.6 Possible Long-term Change in the Conditions of Sedimentation 66

7. IRON, MANGANESE AND RELATED ELEMENTS 68

7.1 Introduction 68

7.2 The Distribution of Iron and Manganese in River and Surface Fjord Waters 68

7.3 The Distribution of Iron and Manganese in Sub-surface Fjord Waters 70

a) O_2-H_2S boundary within the sediment column 70

b) O_2-H_2S boundary at the sediment-water interface 71

c) O_2-H_2S boundary within the water column 72

7.4 The Distribution of Dissolved Manganese in Interstitial Waters 73

7.5 Phase Transformations of Iron and Manganese 73

(A general discussion including:-

Summary of the distributions of iron and manganese 73

Page

7.5 A comparison with iron and manganese distributions in the Black Sea and some lakes 75

Application of models, based on diffusion-advection processes and redox reactions, to explain observed iron and manganese distributions 76

Kinetic considerations of the redox reactions 82

Relationships between the redox reactions and the observed pE/pH conditions). 83

7.6 Discussion of the Nature of the Authigenic Iron and Manganese Phases 84

8. SUMMARY AND CONCLUSIONS 87

APPENDICES

A. General Shipboard Procedure, Sample Collection and Preparation 94

i) General shipboard procedure 94

ii) Determination of geographical position and water depth 94

iii) Water sampling (including sub-sampling and filtration procedure) 95

iv) Coring 97
a) cores for sediment analysis 97
b) cores for interstitial water sampling 98

B. Shipboard Analytical Methods 100

i) Salinity and temperature 100

ii) Dissolved oxygen 101
a) potentiometric method
b) Winkler Method

iii) Dissolved hydrogen sulphide 101
a) potentiometric method 101
b) colourimetric method 102

iv) pH and Eh 102

v) Dissolved phosphate and silicate 103

vi) Titration alkalinity 104

	Page
C. Laboratory Analytical Methods	106
i) Dissolved transition metals (Fe, Mn, Cu, Zn and Ni) in fjord and river waters	106
ii) Dissolved transition metals in interstitial waters	107
iii) Sediment mineralogy	108
iv) Major elements in sediments	108
v) Sulphur and chlorine in sediments	109
vi) Carbonate-C (CO_2) and total-C in sediments	110
vii) Trace elements in sediments	111
viii) Total weight of suspended particulate matter	112
ix) Analysis of suspended particulate matter for Ca, K, Fe, Ti, Si, Al, Mg, P, Mn, S and Cl	112
x) Mineralogy of suspended particulate matter	115
xi) Scanning electron microscopy	115
D. Chemical Analyses	116
i) Hydrographic and hydrochemical data	116
ii) Suspended particulate matter and dissolved metal data	116
iii) Sediment data	116
E. Description of Sediment Cores	120
ACKNOWLEDGEMENTS	123
BIBLIOGRAPHY	125

CHAPTER 1

INTRODUCTION

The geochemical study of strongly reducing (anoxic) sediments initially aroused considerable interest because of its relevance to an understanding of the origin of metal-rich black shales and petroleum. However, there has been an increasing trend for this kind of research to be aimed not at elucidating the connection between anoxic sediments and their ultimate 'geological' equivalents but instead at understanding geochemical processes in recent sediments. In particular this has led to a greater knowledge of both early diagenesis within sediments (in the top 1m of the sediment column) and reactions occurring to inorganic and organic detritus prior to deposition (halmyrolysis). The main marine basins in which this type of study has been carried out are the Black Sea and the fjords of British Columbia and Norway. In many ways, fjords are ideal for the purpose, especially since diagenesis under anoxic and oxic conditions can be compared, while other variables are kept constant. For example, fjords are easily accessible, their circulation is relatively simple, and it is possible to find a fjord containing anoxic sediments and another containing oxic sediments being fed from one source area. Unnatural eutrophication has induced anoxic conditions both within the sediments and overlying waters of many fjords (e.g. Alberni Inlet, see Tully, 1949; Osterfjord, see Ruud, 1968) and has therefore produced an even greater need to comprehend the consequences

of diagenetic changes under such conditions.

One of the most important aspects of research into oxic-anoxic systems is that concerning the distribution of transition metals, in particular manganese and iron. Transformations involving these two metals occur in response to the oxidising or reducing potential of an environment and hence are related to the relative position of the O_2-H_2S boundary. Previous work on this subject (e.g. Bischoff and Ku, 1971; Spencer and Brewer, 1971; Calvert and Price, 1972; Spencer et al., 1972) has been limited to examining the distribution of the two metals either in the water column or underlying sediments, and sometimes to their occurrence only as particulate or dissolved matter. However, the exchange of manganese and iron between the water column and underlying sediments (by gravity settling, diffusion or advection) is of the greatest importance in understanding their distribution. One of the prime objectives of the thesis therefore is to attempt a far more integrated approach to this problem. That is, to study the distributions of dissolved and particulate iron and manganese in both the sediments and overlying waters under a range of redox conditions. The area of study was consequently selected as it contains fjords, according to the data of Gaarder (1916) and Strøm (1936), in which the O_2-H_2S boundary occurs within the sediment, at the sediment-water interface and within the water column.

General circulatory processes in fjords are fairly well-known and the transport of detritus in estuaries and to a lesser extent in fjords has been examined by several researchers. However, little information exists on the chemical composition of suspended particulate

matter and even less about chemical transformations which it may undergo. This aspect of fjord study is no less important than that already discussed, especially since there has recently been increasing concern about the dispersal of pollutants (heavy metals and other industrial pollutants as well as domestic sewage) in near-shore waters. For these reasons, the other main aims of the thesis are firstly, to elucidate the relationship between the distribution of suspended particulate matter and the hydrography and hydrochemistry of the fjords, secondly to determine the nature of the suspended particulate matter including a detailed knowledge of its chemical composition, and thirdly to understand the relationship between its distribution and composition and those of the underlying sediments.

One of the main practical problems faced in a study of a present-day sedimentary environment is its surprising complexity. To understand any one aspect completely it is necessary to have as broad a knowledge as possible of the whole system. The best illustration of this is the important probable role that biological agents play in many diagenetic reactions including manganese and iron redox reactions. This has led to an increasingly broader ('interdisciplinary') approach in research of this kind, as demonstrated by the work of Presley and co-workers in Saanich Inlet (Brown et al., 1972; Nissenbaum et al., 1972; Presley et al., 1972), and is the reason why the scope of this thesis was kept as wide as possible while still concentrating on its main objectives. The sampling necessary for this work was carried out during three cruises of the "Hans Reusch", which belongs to the Geological Institute of the University of Bergen (14-18 October 1970;

15–18 August 1971; 1–3 August 1972). All chemical analyses were carried out either at the time of sampling or later, at the Grant Institute of Geology, Edinburgh. The oxygen analyses in 1972 are an exception in that they were completed at the Geophysical Institute, Bergen.

CHAPTER 2

INTRODUCTION TO THE AREA OF STUDY

2.1 General

The fjords under study are situated between 30 and 55 km to the north-east of Bergen on the west coast of Norway (Fig. 2.1). The fjord system to which they belong is connected at its southern end to the Norwegian Sea. Ground elevation generally increases north-eastwards from Bergen reaching ~1000m in the Mofjord area (Fig. 2.2). Average annual precipitation on the west coast of Norway although high shows considerable local variation. For instance, the yearly precipitation in the catchment areas of Mofjord and the outer Bergen district is 350cm and 150cm respectively (Strøm, 1936).

For the purposes of this study, Mofjord and Osterfjord are subdivided as shown in Figure 2.2 on the basis of their hydrography and bottom sediment geochemistry. Inner Mofjord remains unchanged but the outer basin of Mofjord refers only to that part of the fjord between the inner shallow sill (Mostraumen) and the outer, deeper sill at Fleo. The remainder of Mofjord proper, Romarheimsfjord and Osterfjord are collectively referred to as Osterfjord.

2.2 Geology and Sediment Supply to the Fjords

The geology of part of the area covered by Fig. 2.3 has been described by Kolderup and Kolderup (1940) in the publication 'Geology of the Bergen Arc System'. This System comprises:-

a) The Arcs proper: Cambro-Silurian schists with some Old

Fig. 2.1

MAP SHOWING LOCATION OF THE AREA OF STUDY

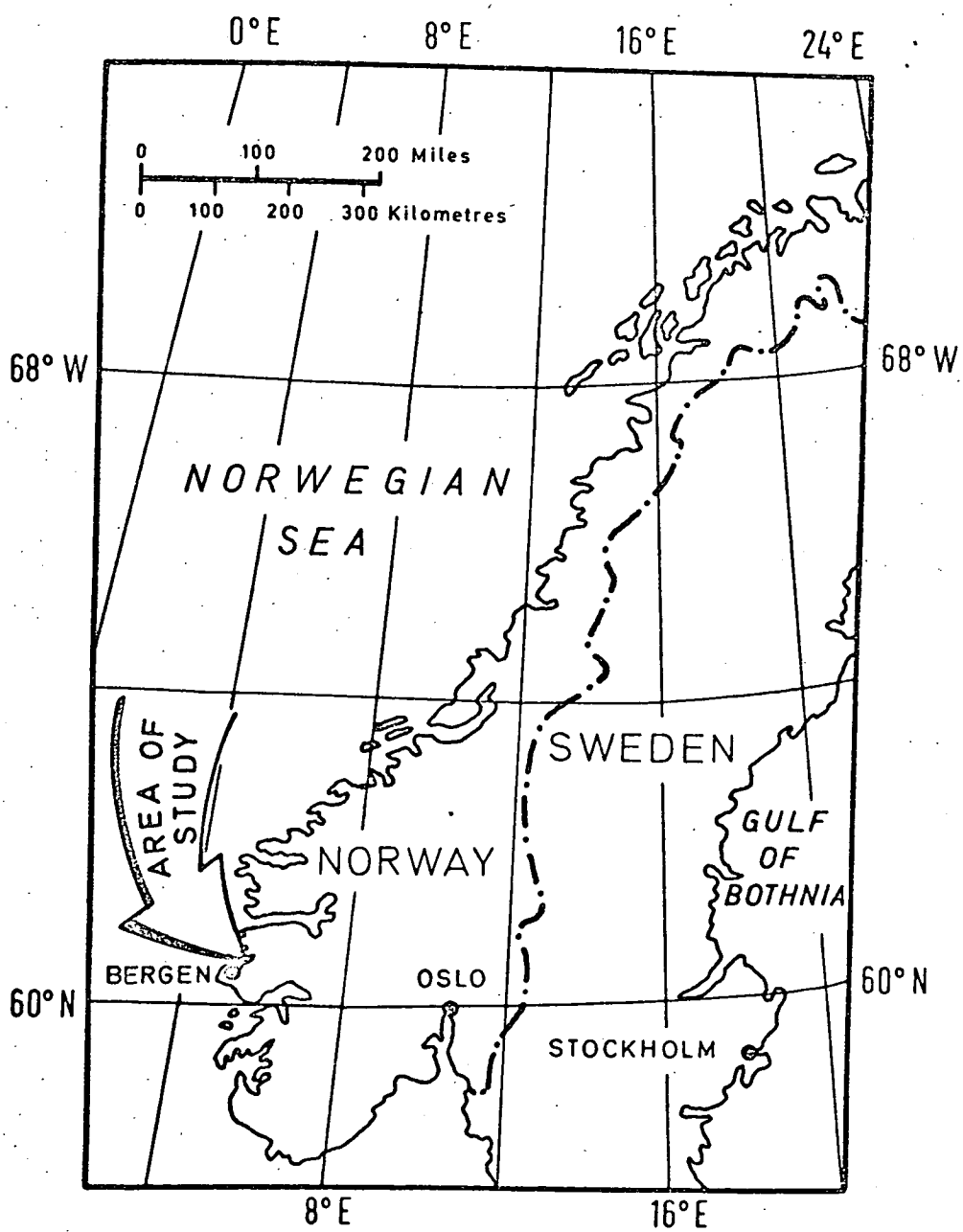


Fig. 2.2 Area of study

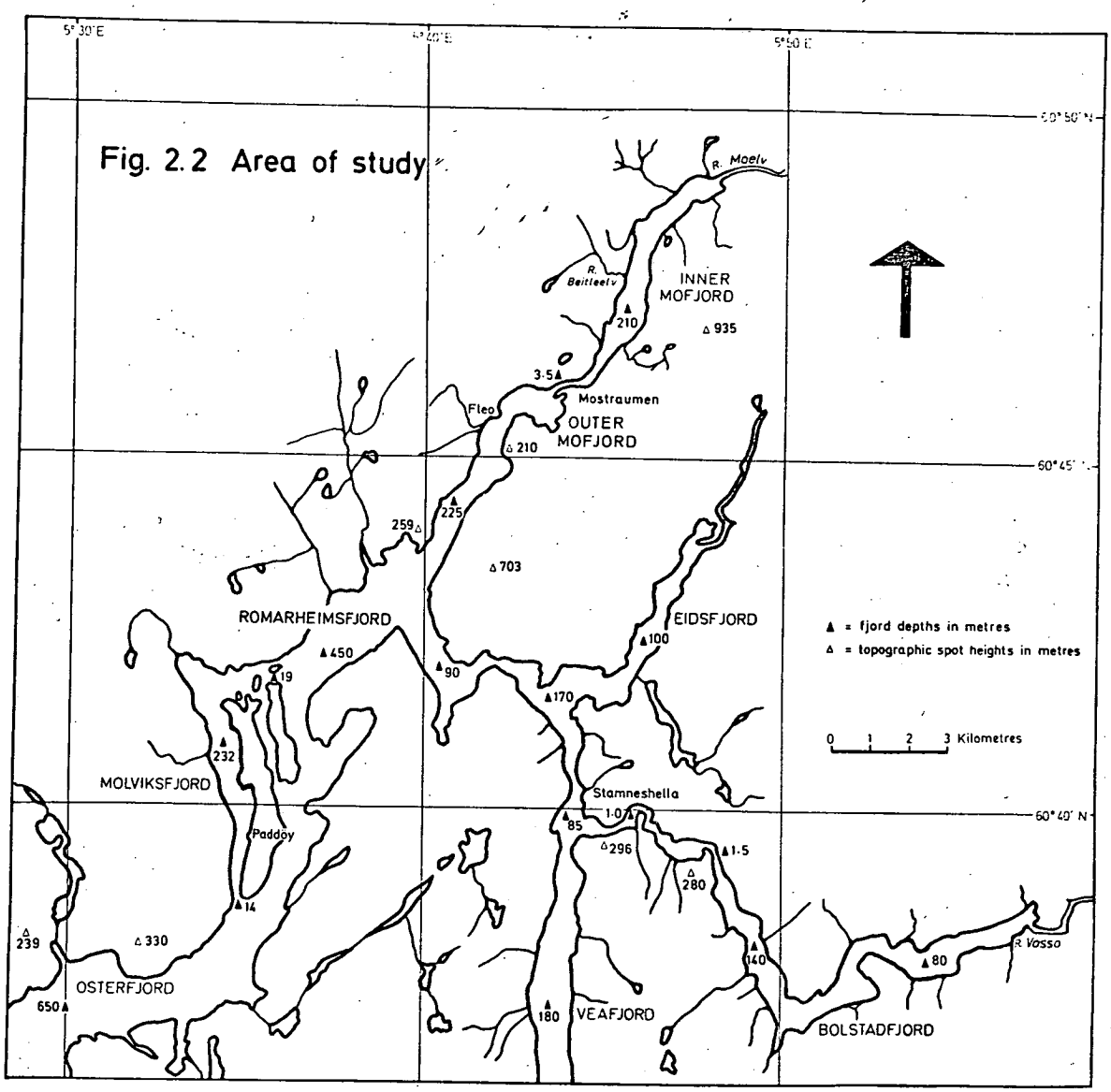
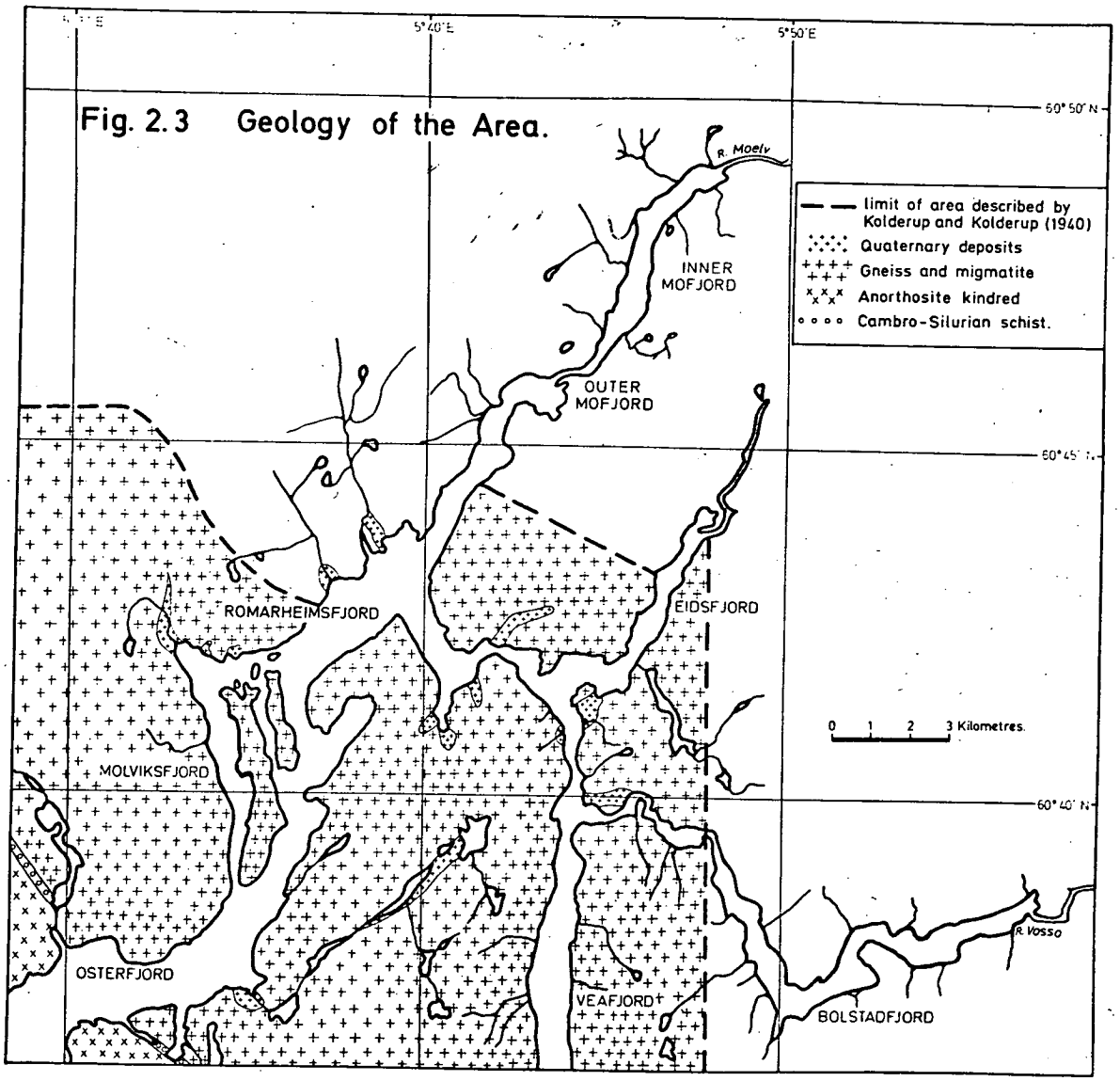


Fig. 2.3 Geology of the Area.



Red and Caledonian igneous rocks. Some of the lesser metamorphosed sedimentary rocks are fossiliferous.

b) The Igneous Rocks of the Anorthosite Kindred.

c) Gneisses of different kinds (migmatites) found in association with granites and gabbros, which are of a variety of ages including Pre-Cambrian.

The bedrock at the northern end of Osterfjord mainly comprises rocks of group c (Fig. 2.3), and preliminary mapping suggests that these rocks extend into the area around Mofjord (Kildal, pers. comm.). However, the small isolated Quaternary deposits (after Kolderup and Kolderup, op. cit.; Fig. 2.3) probably supply a disproportionately large amount of the detritus entering the fjords as they constitute much of the easily eroded material in the area. Transport distances of material forming glacial deposits in Norway are often short (Lag, 1960). Therefore, it is possible that the composition of the bedrock reflects that of the superficial deposits, which in turn will have a very strong influence on the composition of the fjord sediments. Soil cover in this part of Norway is poor but organic-rich (Lag, 1960).

2.3 Geomorphology and Bathymetry of the Fjords

Bathymetric information was largely obtained from published data. However, some spot soundings and single profiles along Mofjord and Bolstadfjord were made with a SIMRAD echo-sounder.

Osterfjord is ~35 km long and varies in width from under 1 km to 3 km (Fig. 2.2). Deep sills divide it into three basins, the deepest one (645m) lies at the southern end of the fjord. The fjord shallows northwards. The local ground elevation increases northwards

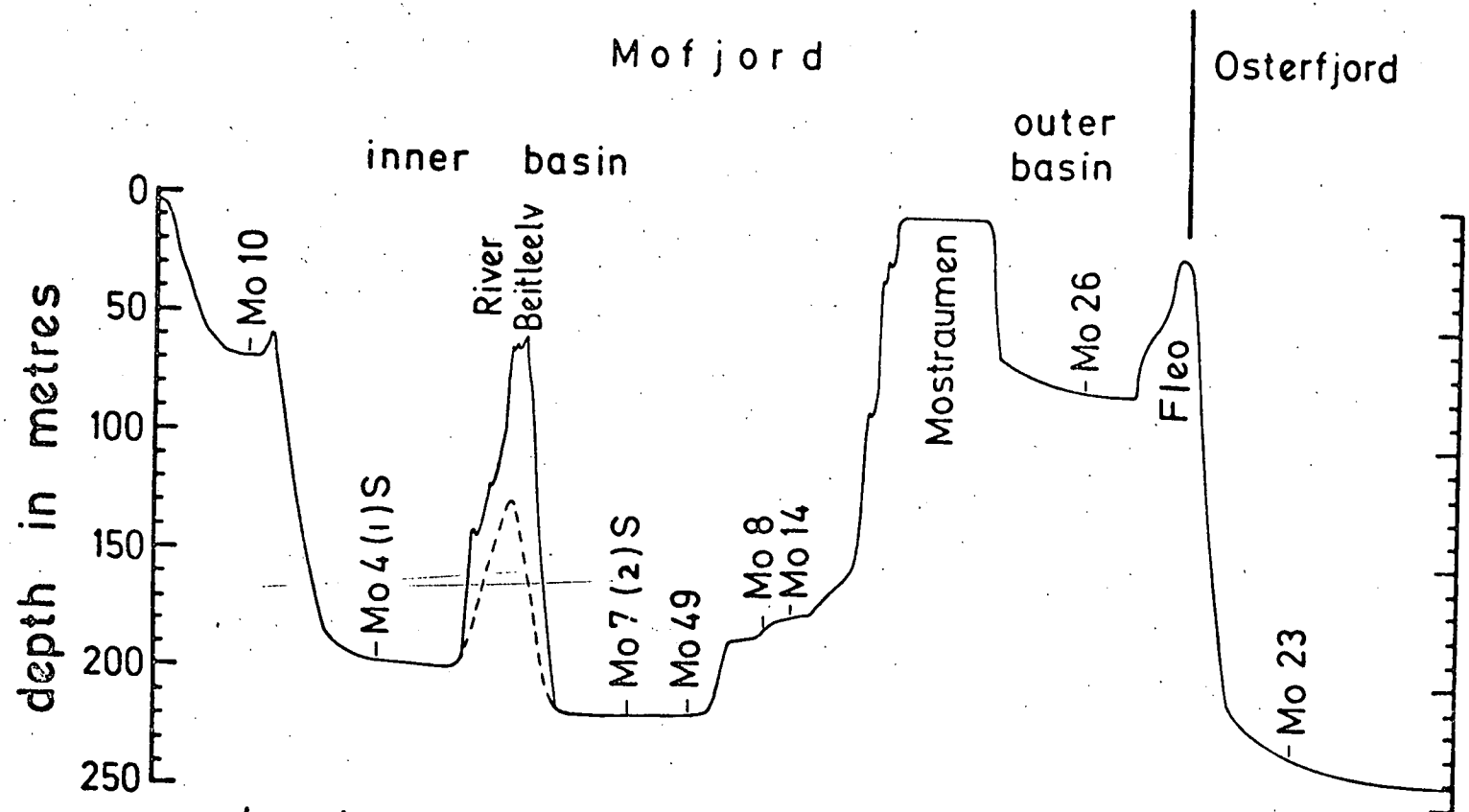
accompanied by a gradual steepening of the fjord walls.

Molviksfjord, situated to the west of the island of Paddöy, is separated from Osterfjord by sills, 14m and 17m, at its southern and northern ends respectively, and has a maximum depth of ~235m.

The sill at Fleo separating Osterfjord from the outer basin of Mofjord is ~15m deep (Strøm, 1936), while the outer basin itself has a maximum depth of ~78m. The inner sill, Mostraumen, is 700m long and is reputed to have been deepened around 1916 from 2m to its present depth of ~3.5m (Strøm, op. cit.). Inner Mofjord is 8 km long and has a relatively constant width (~700m). The northward trends observed in Osterfjord continue into Mofjord so that the walls are even more precipitous, rising almost vertically to ~500m in places. The maximum depth recorded by echo-sounder in the inner basin is 210m, agreeing with local navigational charts (Den Norske Kyst, Sheet 119). Fig. 2.4 shows the depth profile taken along the middle of Mofjord and the northern end of Osterfjord. The sill (60m) shown in the profile within the inner basin of Mofjord and adjacent to the mouth of the River Beitleelv does not represent the true nature of the sill because it slopes down to 125m at the fjord's eastern side.

Bolstadfjord is entered via a 5 km long sill which has a minimum recorded depth of 1m (Strøm, 1936) although it subsequently appears to have been deepened to ~2m. Bolstadfjord is 13 km long, ~600m wide and is divided into three basins by two sills. The depth profile along the middle of the fjord (Fig. 2.5) shows the two sills to be 50m (outer) and 25m (inner) compared, respectively, to maximum

Longitudinal profile of Mofjord and northern end of Osterfjord



Length of profile ~14 km.

Dashed lines after Strøm (1936)

Fig. 2.4

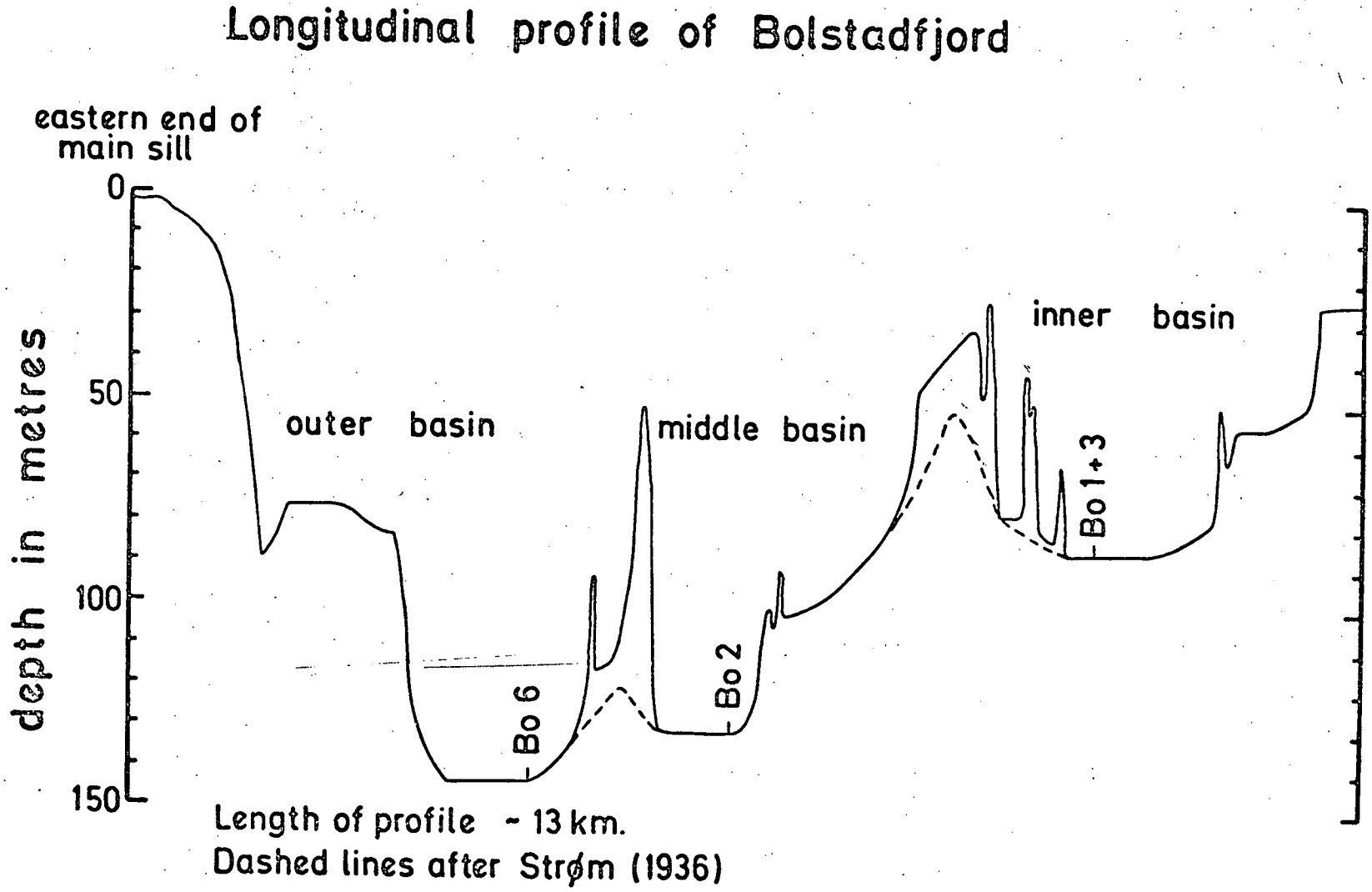

Longitudinal profile of Bolstadfjord
eastern end of main sill
0
50
100
150
depth in metres
outer basin
middle basin
inner basin
Bo 6
Bo 2
Bo 1+3
Length of profile ~ 13 km.
Dashed lines after Strøm (1936)

Fig. 2.5

depths of ~120m and ~52m recorded by Strøm (1936). Therefore, these sills must also vary in depth across the fjord. The deepest point of the fjord occurs in the outer basin (141m), while the maximum depths in the middle and inner basins are ~130m and ~80m respectively.

Osterfjord, Molviksfjord, Mofjord and Bolstadfjord, all fit the definition of a fjord formulated by Pritchard (1952) as an elongated indentation of the coast line containing a relatively deep basin with a shallower sill or threshold at its entrance. Their present form is thought to be due to Pleistocene ice action (Holtedahl, 1960). The geology of the Bergen area controls to some extent the pattern of the fjord system although this is not particularly evident locally. For instance, Osterfjord actually cuts across the structural grain of the country, probably due to the existence and accentuation of a pre-Pleistocene estuary or river valley. The fjords are eroded through physically resistant rocks which explains their narrow and steep-sided nature. It was noted above that the morphology of the main sills (Mostraumen and that at the entrance to Bolstadfjord) is different from that of the 'internal' sills in Mofjord and Bolstad-fjord. Not only are the former much shallower but they also coincide with a particularly narrow section of the fjords. According to Strøm (1936), these two sills represent terminal moraines deposited by receding glaciers. On the other hand, the 'internal' sills do not coincide with a narrowing of the fjords, nor do they usually extend across the full width of the fjords. Significantly, they are located immediately adjacent to where the larger rivers enter the fjords suggesting that they have been built up from deltas in post-glacial times.

CHAPTER 3

HYDROGRAPHY

3.1 Introduction

Various hydrographic and hydrochemical measurements were made at the stations shown in Fig. 3.1. A complete set of tabulated data is included in Appendix D, and analytical methods in Appendices B and C.

The hydrography of the coastal waters is of some interest since it will directly affect that of the fjords. The Baltic current, with its characteristic low salinity, can be traced flowing northwards along the west coast of Norway becoming progressively mixed with Atlantic waters of a higher salinity. In the Bergen area runoff and direct precipitation also affect the salinity of coastal waters so that on balance the fjords have access to waters usually within the limits of 31 to 35‰.

Tidal variation in the area averages ~1m, although in 1933 the difference between the highest and lowest waters was especially great (1.9m) at Bergen as a result of many exceptionally violent storms. The latter conditions caused renewal of the bottom waters of many fjords of western Norway (Strøm, 1936).

3.2 Salinity and Temperature

Salinity and temperature were determined only in the upper 90-120m at each station due to limitations of the N.I.O. salinometer used (see Appendix B).

Profiles of salinity for the various stations, illustrated in

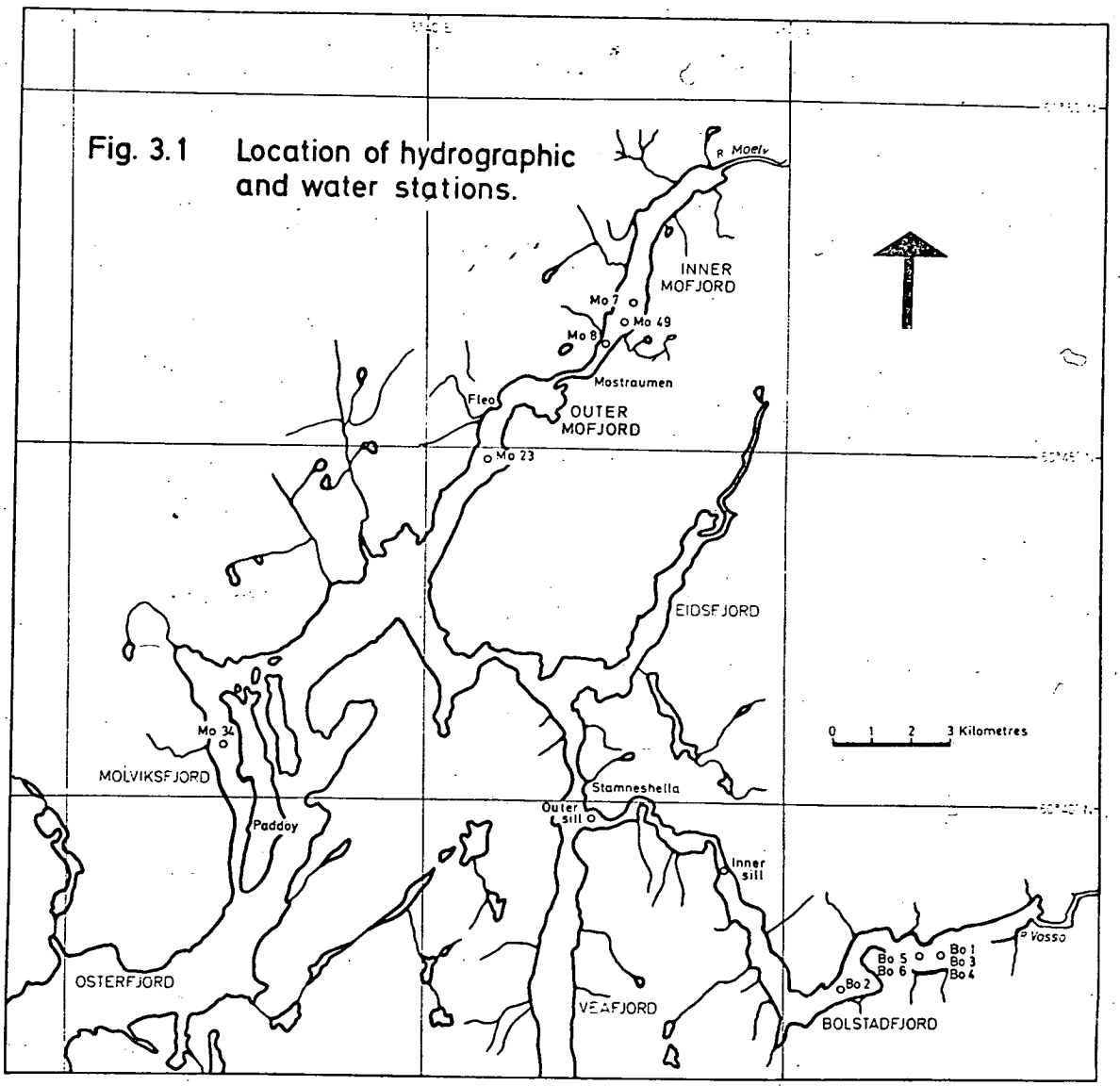


Fig. 3.1 Location of hydrographic and water stations.

Figs. 3.3-3.11, show a well-defined halocline with a positive gradient[1] at or near to the surface. The low salinity of the surface waters is the result mainly of local runoff but may be exaggerated by direct precipitation. Such a feature is characteristic not only of fjords (e.g. Pickard, 1961; 1963b; Herlinveaux, 1962; Rattray, 1967; Saelen, 1967) but estuaries in general (e.g. Bowden, 1967; Pritchard, 1967). No current measurements were made but it was observed from the drifting of leaves that the surface waters invariably flowed seawards.

The near-surface salinity profile observed at all stations and the omnipresent surface outflow indicate the most common type of surface water circulation found in fjords, namely 'two-layer flow with entrainment', where sub-surface inflow occurs to compensate for salt water entrained by the outflow (Bowden, 1967). Thus salinity is a conservative parameter whose distribution is controlled by mixing between low salinity surface water and underlying high salinity water. Fig. 3.2a shows diagrammatically the probable surface circulation.

A thermocline, usually with a negative gradient, is always coincident with the halocline (Figs. 3.3-3.11). However, it is the very marked change in salinity that is always the dominant control on density distribution as in most estuaries (Pickard, 1963a). Therefore, a marked pycnocline (density gradient) invariably coincides with

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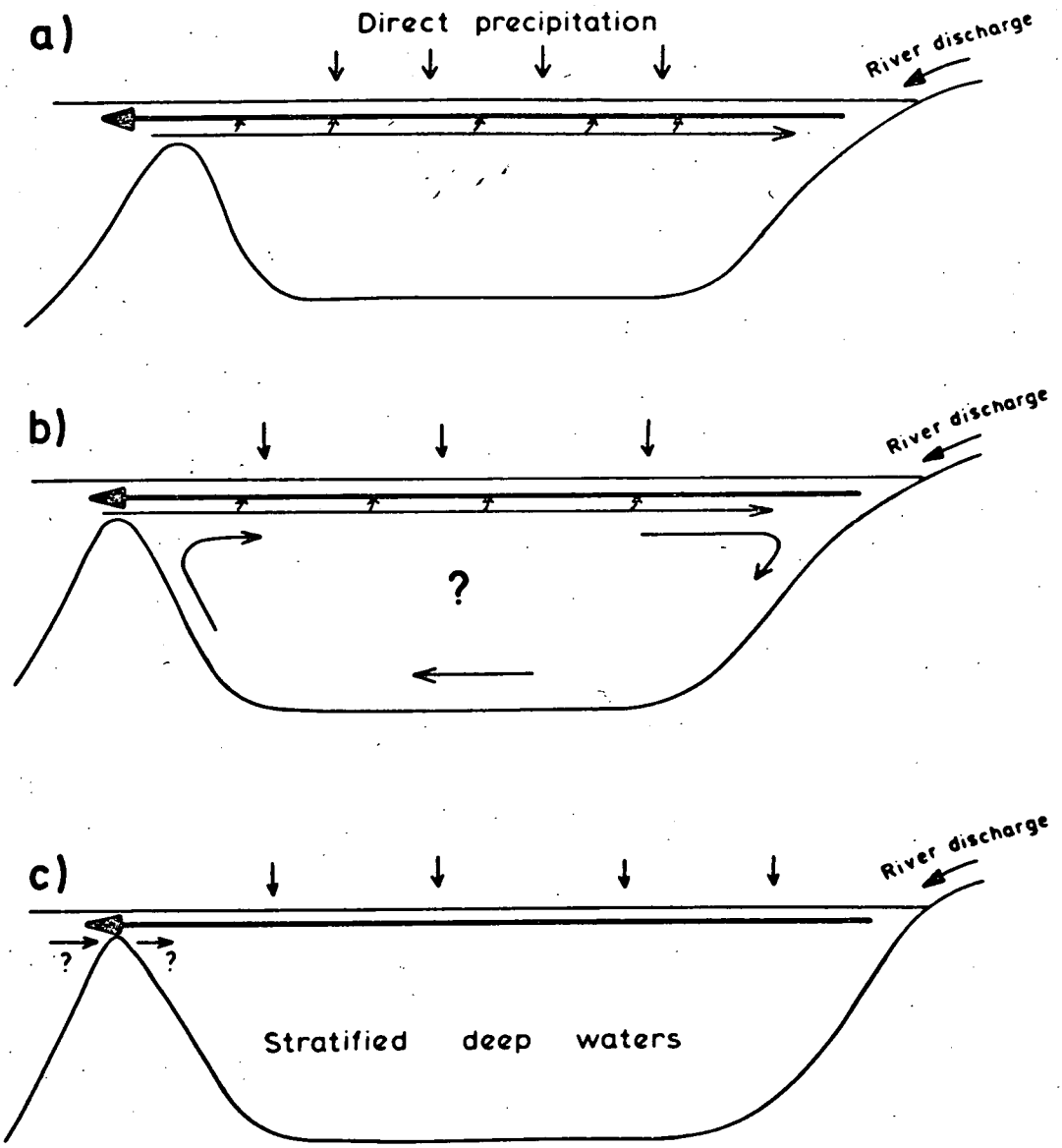
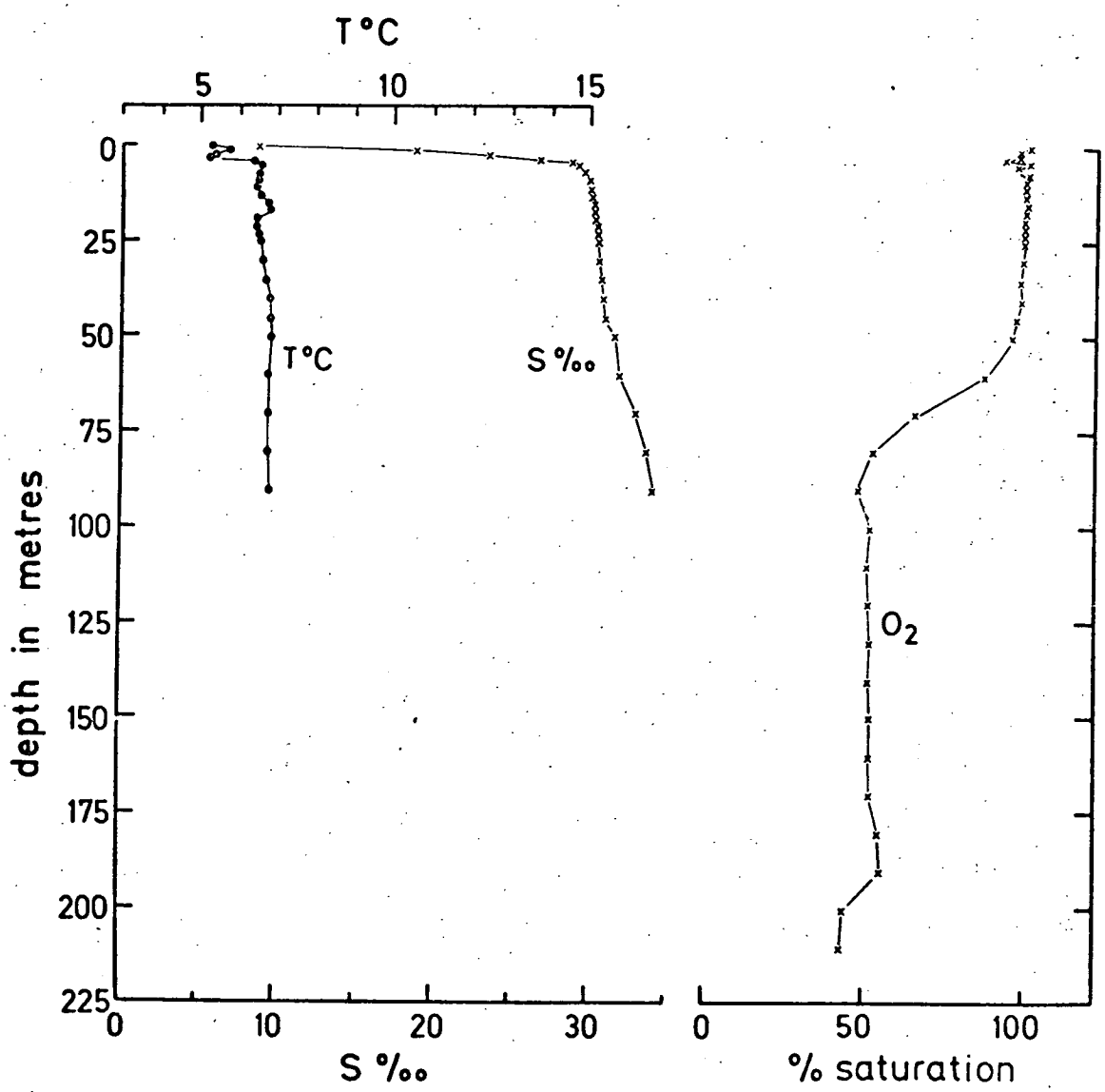
1 A positive gradient of a parameter is defined as an increase in its concentration with depth.

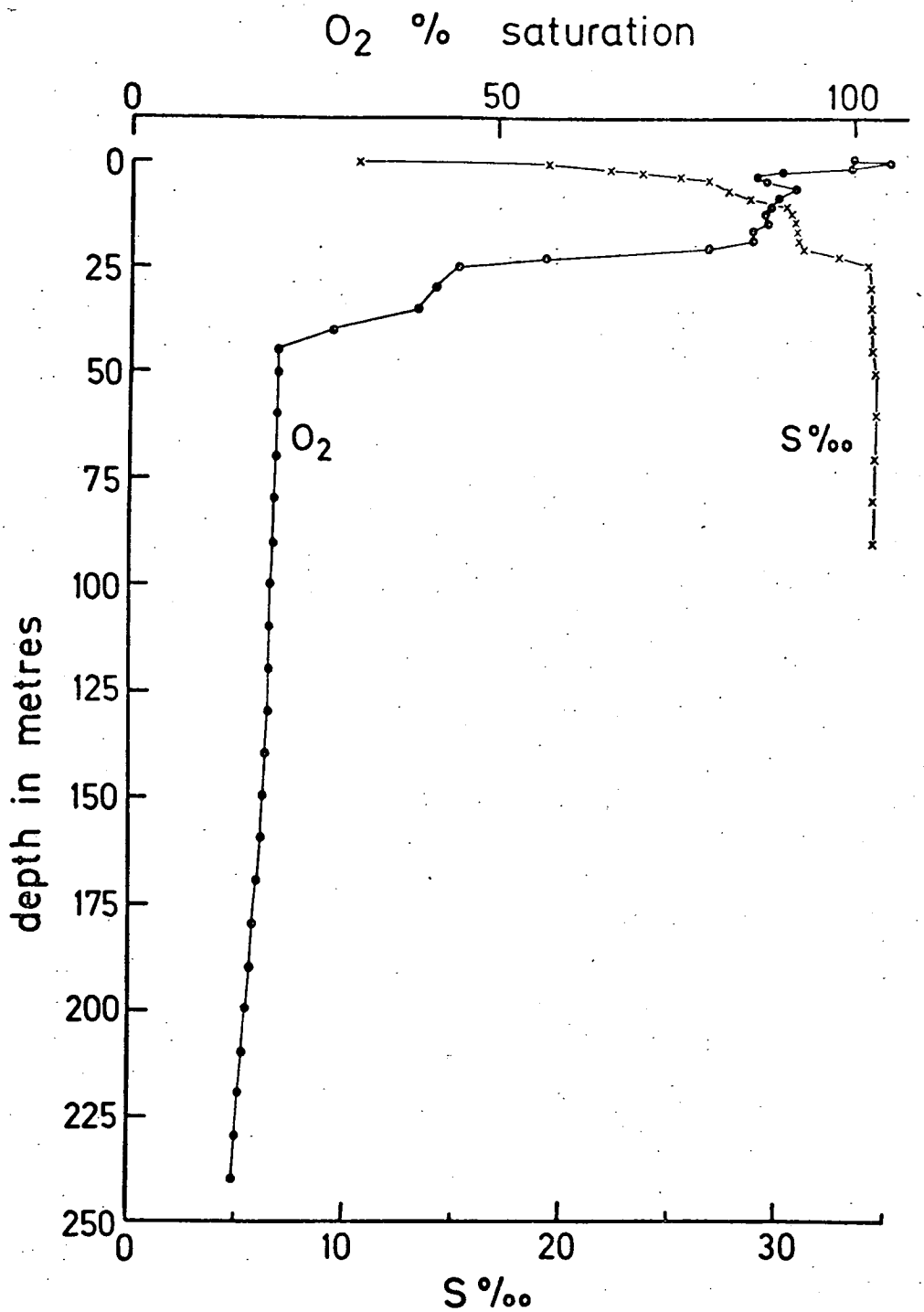
FIG. 3.2 Idealised Circulation Patterns





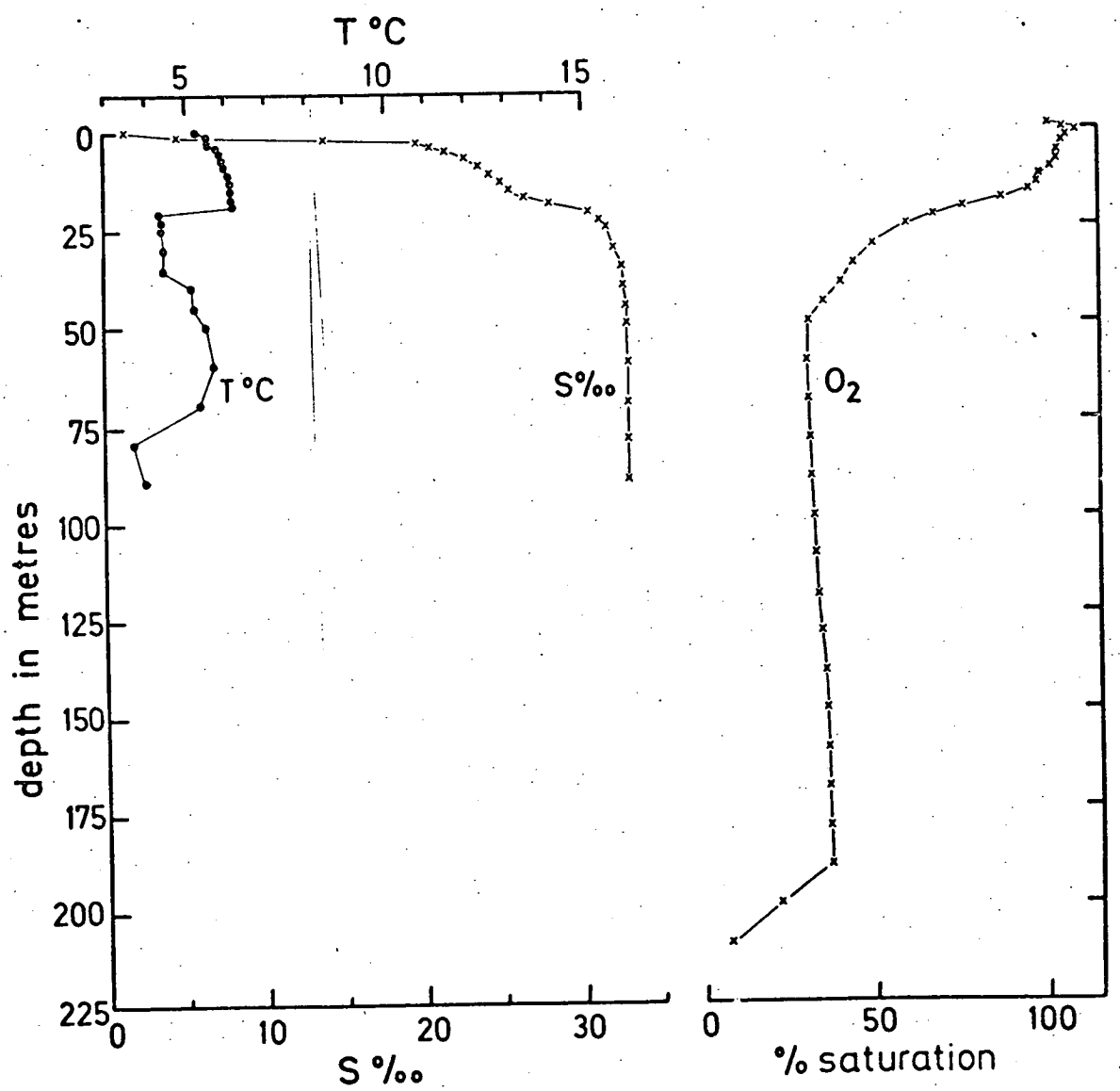
Salinity, temperature and dissolved O_2 profiles at Mo 23, Osterfjord

Fig. 3.3



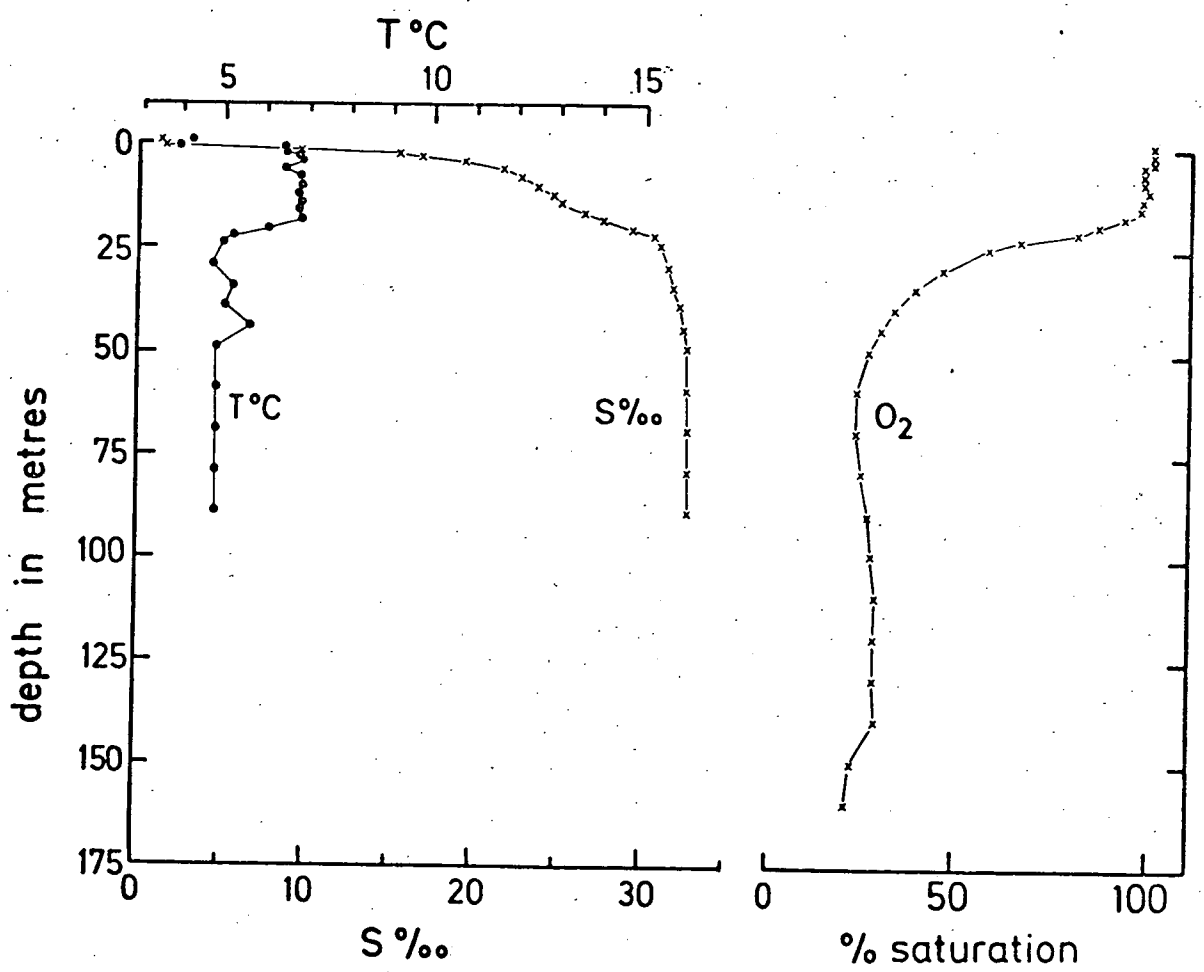
Salinity and dissolved O_2 profiles at Mo 34, Molviksfjord

Fig. 3.4



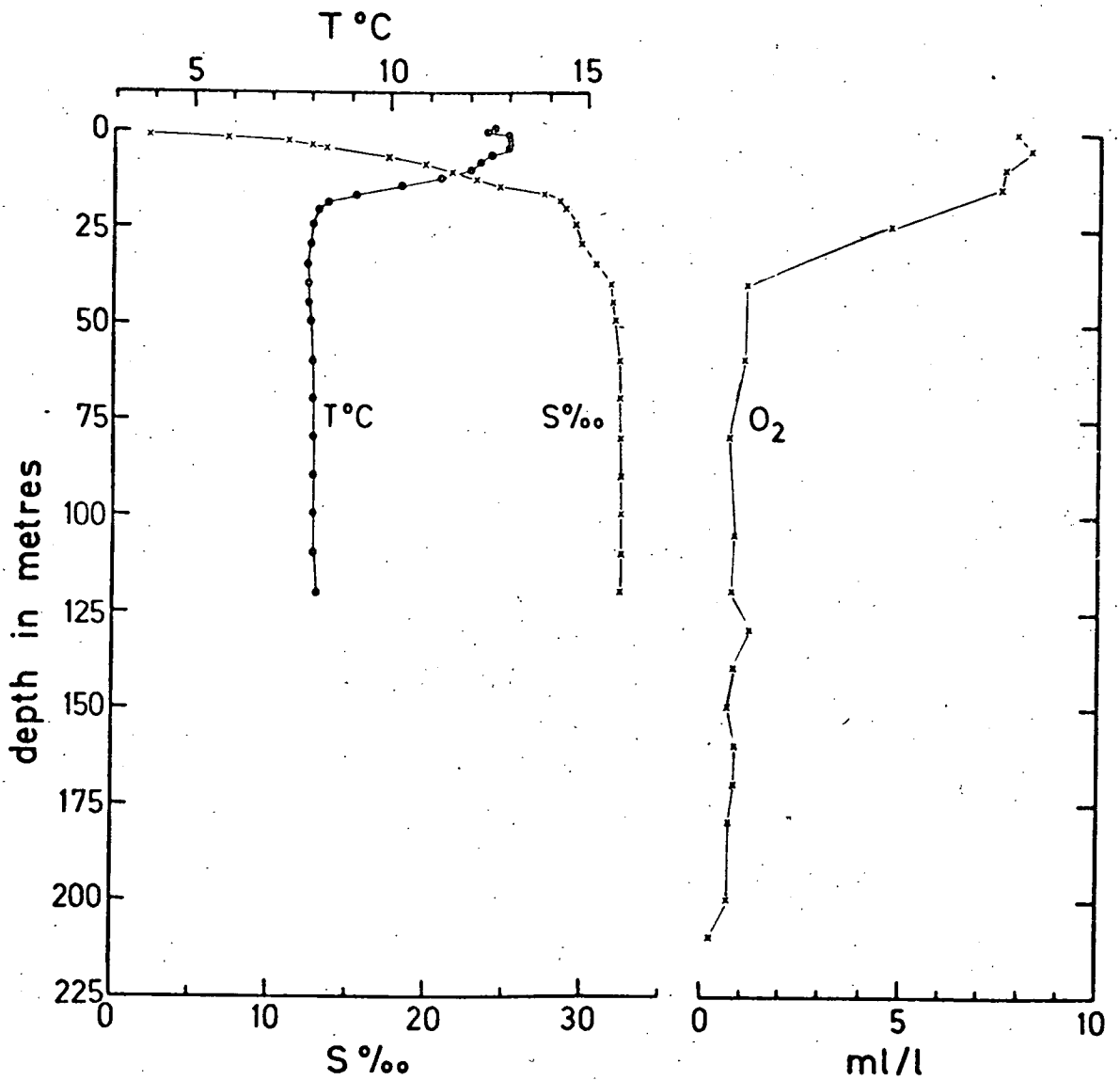
Salinity, temperature and dissolved O_2 profiles at Mo 7, Mofjord

Fig. 3.5



Salinity, temperature and dissolved O_2 profiles at Mo 8, Mofjord

Fig. 3.6

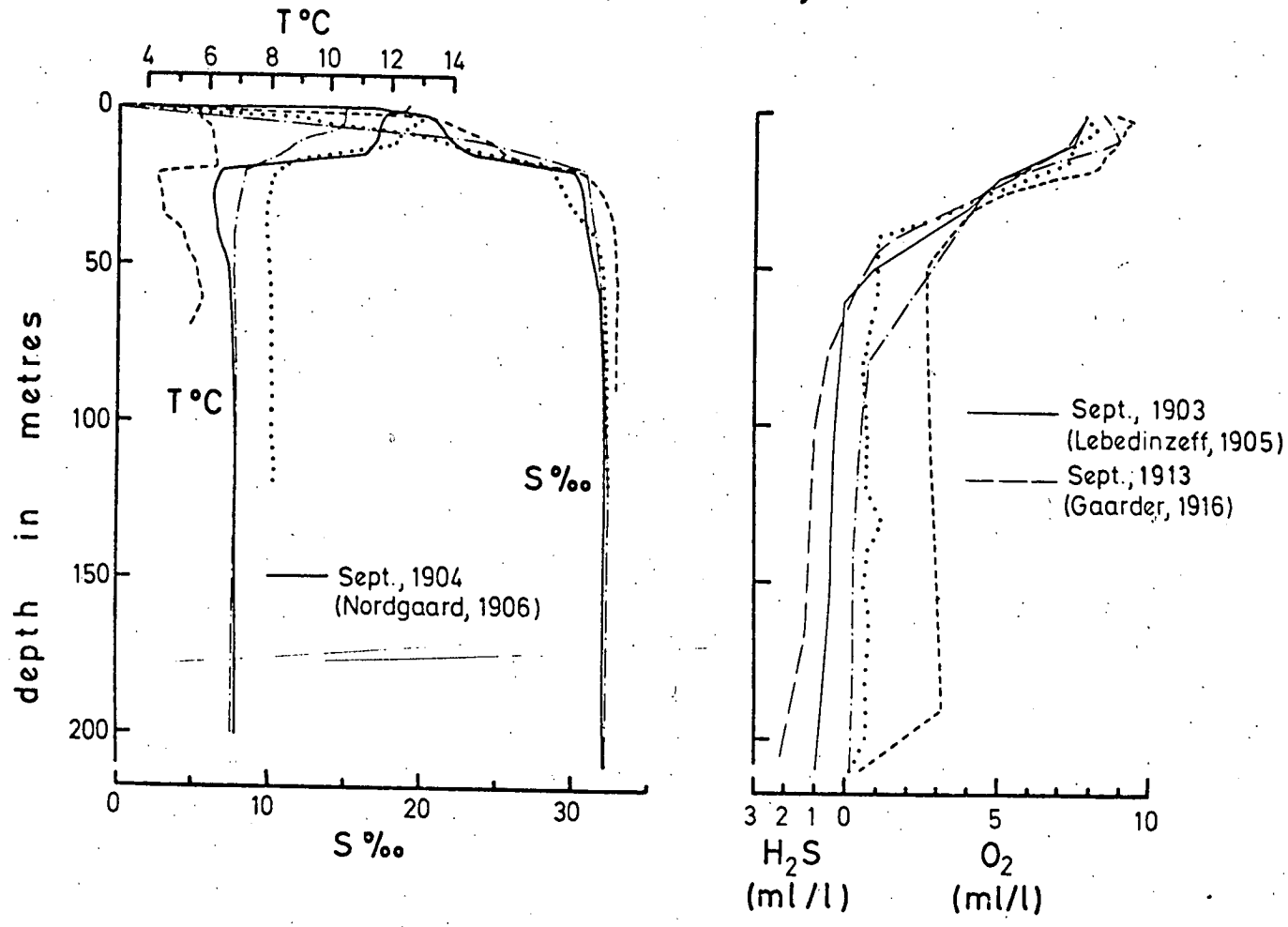


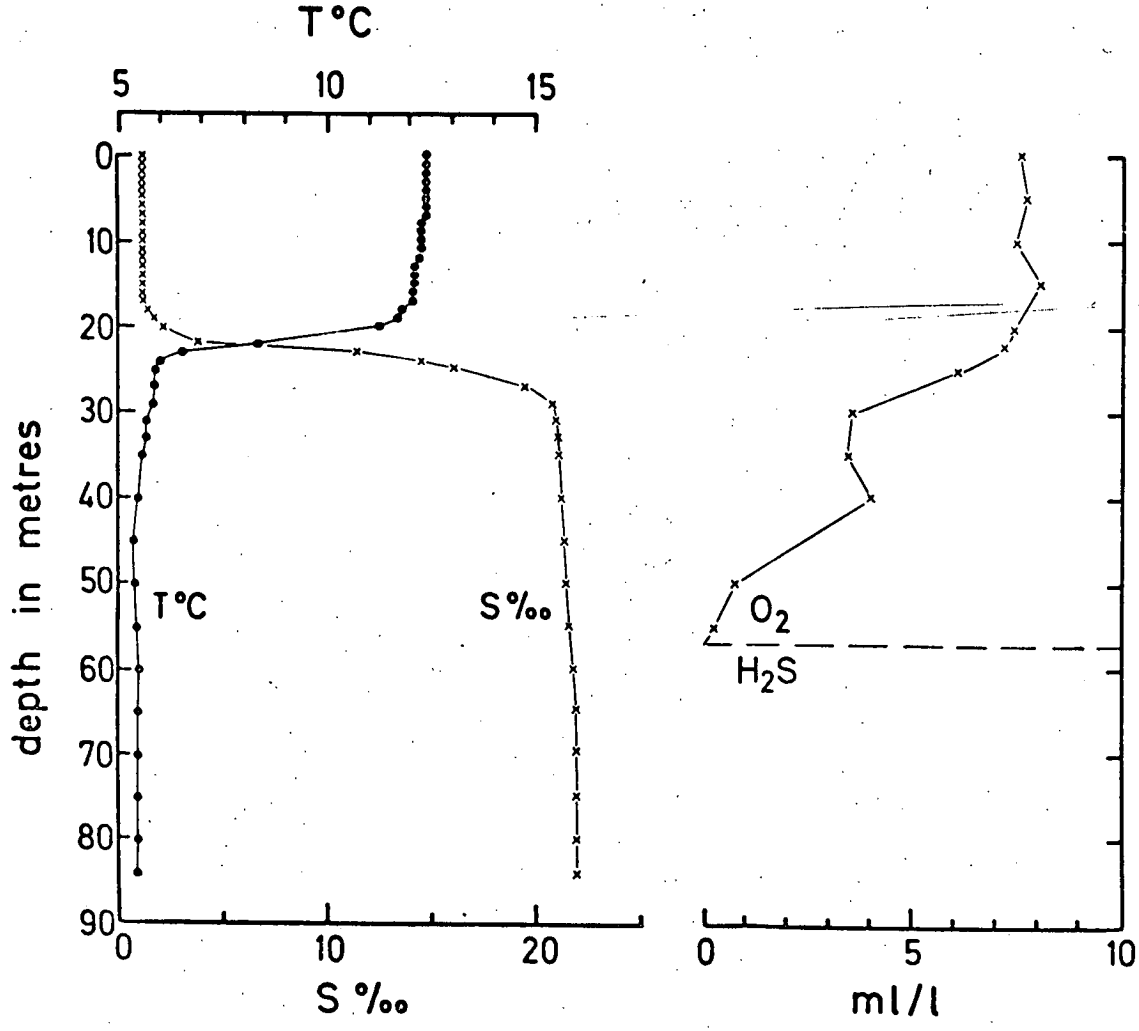
Salinity, temperature and dissolved O_2 profiles at Mo 49, Mofjord

Fig. 3.7

Fig. 3.8

Comparison of salinity, temperature and dissolved O_2 / H_2S profiles at the deepest point in Mofjord.

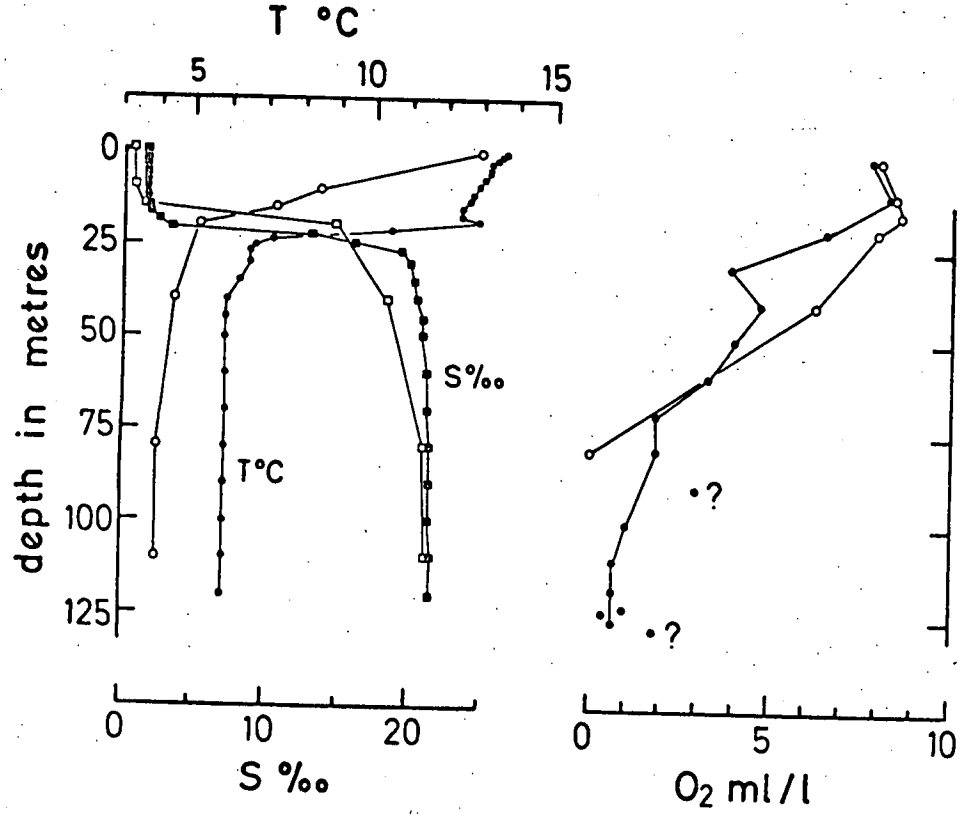




Salinity, temperature and dissolved O_2 profiles at Bo 1, Bolstadfjord

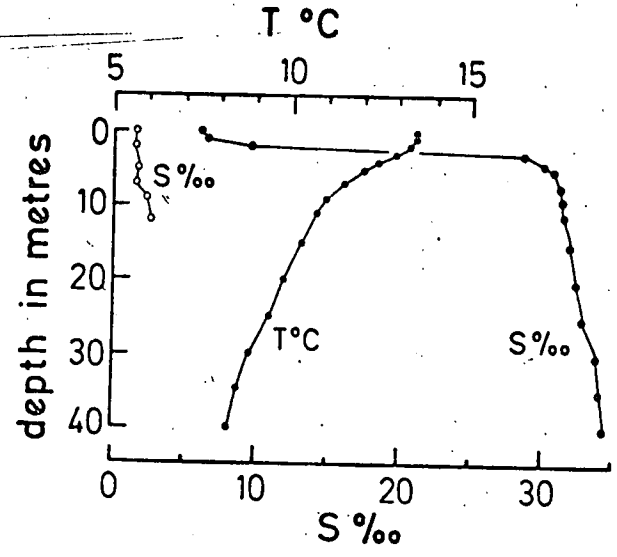
Fig. 3.9

Fig. 3.10



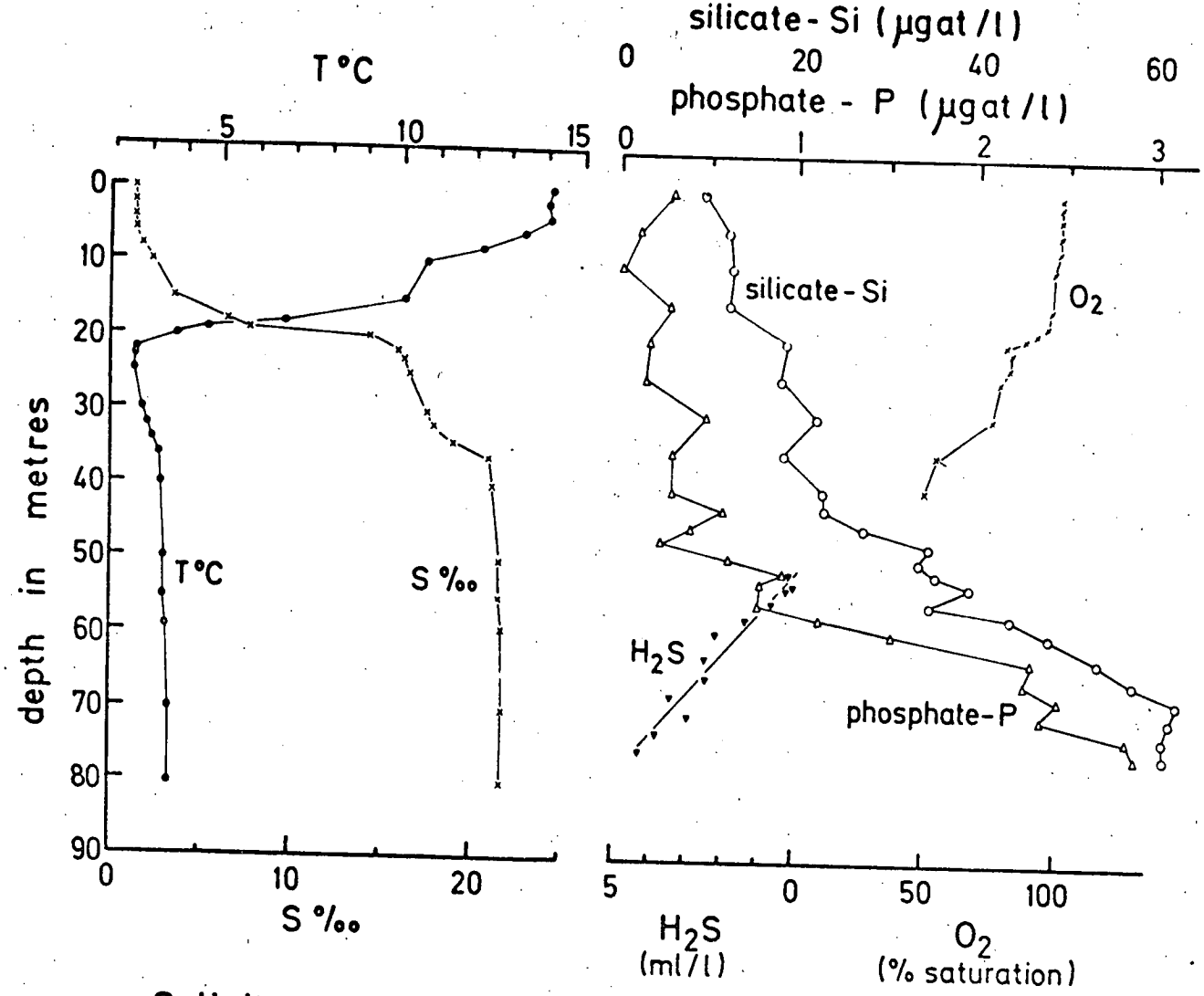
□ ○ = After Strøm (1936)

Salinity, temperature and dissolved O_2 profiles at Bo 2.



• = outside sill
○ = inside sill

Salinity and temperature profiles at the sill stations.



Salinity, temperature, dissolved O_2, H_2S, phosphate-P and silicate-Si at Bo 4, Bolstadfjord

Fig. 3.11

the main halocline.

Salinity and temperature distributions within the deeper waters vary considerably between fjords and will be discussed below.

3.3 Dissolved Oxygen

As dissolved O_2 was analysed using an 'oxygenmeter' in 1970 and 1972 (see Appendix B), and by Winkler titration in 1971, the data are presented in terms of percentage saturation relative to the surface water concentration[2] and in units of ml/l O_2 respectively. This makes direct comparison of the two sets of data difficult although trends may be compared reasonably well. The difficulty arises largely from non-equilibrium of O_2 between surface waters and the atmosphere. This may be demonstrated by calculating percentage saturation using the more common method of expressing the observed concentration as a percentage of the equilibrium concentration at in situ temperature and salinity at 1 atmosphere pressure. Table 3.1 shows the observed and calculated dissolved O_2 concentrations at stations Mo 49, Bo 1 and Bo 2. Evidently, the surface waters at all three stations are supersaturated and are therefore losing O_2 to the atmosphere. This in part is due to the upward flux of O_2 from a maximum at depths between 1m and 15m (Figs. 3.7, 3.9 and 3.10). A similar maximum is present at two of the stations occupied in other years (Figs. 3.4 and 3.5). Such a maximum is common in fjords (e.g. Strøm, 1936; Gaarder, 1916; Pickard, 1961) and most other types of

2 This definition of saturation is used throughout unless otherwise stated.

TABLE 3.1

A comparison of equilibrium O_2 concentrations at 'in situ' conditions with observed concentrations at stations Mo 49, Bo 1 and Bo 2

Station	Depth (m)	Equilibrium concentration (ml/l)	Observed concentration (ml/l)
Mo 49	1	7.36	7.86
	5	6.80	8.23
	10	6.65	7.62
	15	6.79	7.42
	25	6.95	4.70
	40	6.87	1.03
	60	6.87	1.00
	80	6.86	0.60
	105	6.85	0.76
	120	6.85	0.68
	130	6.85	1.15
	140	6.85	0.74
	150	6.85	0.58
	160	6.85	0.79
	170	6.85	0.78
	180	6.85	0.63
	200	6.85	0.67
	210	6.85	0.20
Bo 1	0	7.48	7.53
	5	7.48	7.72
	10	7.48	7.47
	15	7.50	7.99
	20	7.62	7.38
	22	8.05	7.12
	25	7.91	5.99
	30	7.83	3.53
	35	7.74	3.42
	40	7.74	3.93
	42.5	7.74	3.05
	45	7.74	3.12
	47.5	7.74	1.80
	50	7.74	0.70
	52.5	7.74	0.70
	55	7.74	0.20
Bo 2	0	7.20	7.79
	10	7.34	8.28
	20	7.52	6.47
	30	7.64	3.85
	40	7.64	4.65
	50	7.64	3.97
	60	7.64	3.21
	70	7.64	1.80
	80	7.64	1.80
	90	7.64	2.91
	100	7.64	1.00
	110	7.64	0.70
	118	7.64	0.70
	123	7.64	1.00
	124	7.64	0.40
	127	7.64	0.70
	129	7.64	1.80

water body, and is usually attributed to the activity of photo-synthesising organisms. Abundant diatoms were collected in the near-surface waters of Mofjord and Bolstadfjord (p. 33) suggesting that the observed maxima have a similar origin. Heating of surface waters lowers the O_2 solubility and therefore is also capable of producing a sub-surface dissolved O_2 maximum (Strøm, 1936; Richards, 1957). However, this mechanism is considered to be unimportant in causing the observed maxima as the near-surface temperature and salinity conditions are such that, except at Bo 2, a surface rather than a sub-surface O_2 maximum would result.

There is at least one distinct oxycline with a negative gradient at all stations and, except for Osterfjord, the deep waters are less than 25% saturated with O_2. Variations in the distribution of O_2 often occur at the same depths as salinity and temperature changes, particularly in near-surface waters (Figs. 3.3-3.11). Unlike salinity and temperature, dissolved O_2 is a non-conservative parameter, that is to say its distribution is not only a function of physical transport and mixing but also of <u>in situ</u> production (photo-synthesis) and utilisation. Its depletion in deep waters is due to the oxidation of organic debris by respiring organisms coupled with a lack of circulation.

3.4 <u>Osterfjord</u>.

In Osterfjord (station No 23, Fig. 3.3), the low salinity water is restricted to the surface 4m owing probably to a lessened influence of river discharge, the great width of the fjord, and greater mixing between surface and deeper waters. At 45m depth, there is a significant

change in the salinity gradient, and this also marks the upper boundary of an isothermal water body. No sub-surface O_2 maximum exists. Oxyclines between 50-80m and 190-200m separate the water column into three units, each having constant dissolved O_2 concentrations. The upper 50m is well-oxygenated and even the deepest waters are more than 40% saturated. Gaarder (1916) also observed greater than 90% saturation in the waters of Osterfjord down to ~60m.

The above data suggest the existence of three relatively homogeneous water bodies, separated by zones of mixing, in addition to the low salinity, surface layer. Most of the surface outflow probably occurs in the upper 4m of low salinity water while the surface water circulation, including the compensating current, is probably confined to the upper 50m. The fairly well-oxygenated deep waters indicate a reasonably efficient circulation there too which is only to be expected from the lack of shallow sills in the fjord. Gaarder (1916) found evidence in the fjord for a complex deep circulation and in addition noted its variation with time.

3.5 Molviksfjord

The waters down to 25m depth in Molviksfjord differ from those in Osterfjord in that they show a 'stepped' halocline (station Mo 34, Fig. 3.4). Salinity increases very slowly with depth from 25m to 45m and is then constant to at least 90m. An O_2 maximum is encountered at 1m. Below this there is a 'stepped' O_2 profile to 45m even more complicated than that of salinity. These waters are considerably less aerated than at equivalent depths in the main fjord (Fig. 3.3), for

instance water at 45m is only 20% saturated with O_2. The O_2 content decreases only slowly with depth beneath this to ~15% saturation at 240m.

The main outflow probably occurs in the upper 2m but the surface circulation is obviously complex. It is interesting to note that the steepest part of the salinity gradient occurs above the sill depths (i.e. 14m and 17m). A surprising feature concerning the deep waters (>45m), which comprise 80% of the water column, is that they are well-mixed despite having a restricted circulation as seen from dissolved O_2 concentrations. The O_2 profile also indicates that advection of individual water bodies into the fjord from outside the sill does not often occur. This suggestion is further supported by water in Osterfjord which has a salinity of 30.2‰ at sill depth (17m) compared to water with a salinity of 30.5‰ at the same depth within Molviksfjord. The difference between these two salinity profiles increases with depth, for instance at 10m below sill depth, Osterfjord waters have a salinity of 30.5‰ and Molviksfjord waters a salinity of 33.85‰ . Thus the cause of the deep water mixing within Molviksfjord must be internal. The driving force for this internal circulation may be frictional stress at the upper surface of the deep water body (Rattray, 1967). This is diagrammatically represented in Fig. 3.2b. Certainly in many cases fjords with large river runoff have a greater overall deep water circulation compared to those with a small runoff (Pickard, 1963a).

3.6 Mofjord

An almost homogeneous layer of very low salinity (1.00-1.85‰)

is present in the surface metre of the water column at stations Mo 8 and Mo 49 (Figs 3.6 and 3.7). Both Nordgaard (1906) and Strøm (1936) have already demonstrated the great influence that the River Moelv has on the salinity of the surface waters of Mofjord and recorded a seasonal variation in surface salinity of only 1.01-5.75‰. This implies that runoff is probably sufficient to maintain a permanent density stratification of the surface waters.

Data from 1970 and 1971 show that the main halocline is 'stepped' (Figs. 3.5, 3.6 and 3.7) and the salinity constant with depth between 50m and 120m. Nordgaard (1906) (Fig. 3.8) and Strøm (1936) reported isohaline waters below 100m and noted that the salinity of bottom waters at the deepest part of the fjord ranged between 32.16 and 32.49‰, similar to the values observed in this study (32.10‰ and 32.94‰). Therefore, it seems that little if any long term variation in the salinity distribution has occurred. A comparison of temperature data for the years 1904 (Nordgaard, op. cit.), 1970 and 1971 (Fig. 3.8) shows that there is commonly a surface minimum and a thermocline with a negative gradient somewhere between 5m and 22m. There is a sub-surface O_2 maximum (2-5m) at stations Mo 7 and Mo 49. The main oxycline occurs between limits of 15m and 60m at all stations sampled in the fjord (Figs. 3.5, 3.6 and 3.7). Below 60m O_2 concentrations change little except in the bottom 10-20m of the water column at both the deep stations (Mo 7 and Mo 49) and the shallower station (Mo 8) where there is an appreciable decrease. A point of interest arises from a comparison of O_2 data of this and previous studies, some of which were conducted prior to the deepening

of the main sill in 1916. Lebedinzeff (1905) (Fig. 3.8) and Gaarder (1916) observed that O_2 decreased to zero at 60m below which dissolved H_2S existed reaching a maximum of 2.0 ml/l at 210m. However, the bottom water in June 1932 contained 0.22 ml/l O_2 (Strøm, 1936), similar to that at the present time. Clearly, only prior to deepening of the sill were the deep waters anoxic. Despite this major change in conditions, the depth of the base of the main oxycline (~60m) has remained constant with time (Fig. 3.8).

The data indicate that the fresh water outflow exists primarily in the surface metre or so and the compensating inflow above 25m. The deep waters (>60m) are similar to those in Molviksfjord in that they are surprisingly well-mixed despite the presence of a particularly shallow sill (~3.5m) and a restricted deep circulation as indicated by their low O_2 content. Again there is no evidence to support flushing of the fjord's deep waters by water entering over the sill so that the same arguments can be made in support of some kind of deep internal circulation.

3.7 Bolstadfjord

A very low salinity (~1‰) surface layer up to 20m thick occurs in the inner parts of Bolstadfjord (Figs. 3.9, 3.10 and 3.11). While several significant rivers flow into the fjord, most runoff originates from the River Vosso situated at the fjord's eastern end. Strøm (1936) has estimated its discharge as >80m^3/sec over a period of a year which is of the same order as the rivers supplying the fjords of British Columbia (Pickard, 1961). In 1971 the surface waters were isohaline to a depth of 13m and 10m at stations Bo 1 and Bo 2

respectively (Figs. 3.9 and 3.10). Since river waters are added to the fjord waters between these two stations (Fig. 3.1) and the fjord is wider at Bo 1 than at Bo 2, the thinning of the isohaline layer away from its source indicates that mixing or more correctly entrainment of saline waters by the surface outflow (Pickard, 1963a) increases westwards. Very pronounced haloclines exist between 17-29m and 17-27m at Bo 1 and Bo 2 respectively, indicating that the thickness of the surface outflow is almost constant in this part of the fjord despite entrainment. These features are in accordance with the characteristic surface situation in many well-stratified estuaries, namely that an increase in volume of the surface outflow away from the main source (due to further addition of runoff and to entrainment) does not cause a thicker outflow but one of increasing velocity (Pickard, 1963a).

Both stations (Bo 1 and Bo 2) display only a slight increase in salinity below the halocline. It is important to note that the salinity gradient between 30m and 70m at Bo 1 is slightly less than at Bo 2 suggesting that the waters are fractionally better mixed. The salinity is constant below 70m and 110m at Bo 1 and Bo 2 respectively. There were three significant differences between the 1971 and 1972 salinity profiles for the inner basin. In 1972 (at Bo 4 - Fig. 3.11, and Bo 5):-

a) only the top 5m of the water column was isohaline.

b) the halocline was located over a greater depth range (5-36m).

c) the halocline was 'stepped'.

Although river discharge was almost certainly lower in 1972, it is not

necessarily illustrated in the salinity profiles since the depth of low salinity water is not necessarily dependent on the amount of river discharge. For instance, Tully (1949) found in fjord-like basins that the thickness of the low salinity layer was inversely related to the amount of runoff up to a critical value and thereafter became proportional.

The surface water temperature at station Bo 1 in 1971 was constant at 12.2°C to a depth of 17m whereas at Bo 2, further from the main source of runoff, a small gradient existed between 0m (13.6°C) and 17m (12.4°C), (Figs. 3.9 and 3.10). This feature is interpreted as the increasing effect of solar and atmospheric warming which has also been observed in fjords of British Columbia (Pickard, 1961). At both stations a negative thermocline is coincident with the halocline and below ~40m the waters are essentially isothermal. The temperature distribution within the inner basin in 1972, like that of salinity, shows three important differences from the previous year (Figs. 3.9 and 3.11):-

a) a continuous negative gradient exists between 4m and 21m with a decreased gradient between 10m and 15m.

b) a temperature minimum is present between 22m and 36m.

c) a small positive gradient exists below 36m that is probably due to conduction of heat from the deep waters towards the temperature minimum.

The temperature minimum coincides with the lower part of the 'stepped' halocline indicating that this zone (22-36m) is not one of mixing between adjacent water bodies but represents a third, distinct

water body.

Strøm (1930) occupied a station in the outer basin on a different occasion from that described above and observed similar salinity-temperature conditions to those present in 1972 within the inner basin. Therefore on the four occasions the fjord has been examined, two contrasting types of temperature-salinity profile have each been seen twice implying a recurrent and perhaps even regular change in the fjord's hydrography. Whether this variation is a short term one, perhaps related to tidal change, or a longer term feature, such as a seasonal change, is unknown.

A station immediately inside the sill, occupied in 1971 (Fig. 3.10), shows that low salinity water was present throughout the water column (12m) suggesting that no flow of saline water into the fjord was occurring at the time. Outside the sill (Fig. 3.10), a brackish layer (~5‰) with a relatively high temperature existed in the surface metre. The main halocline occurred between 1m and 3m whereas the temperature decreased steadily below 1m. The sill obviously acts as a barrier to circulation since the maximum density (σ_t) observed within Bolstadfjord is 17.3 compared, for example, to a value of 26.7 at 40m outside the sill. Furthermore the water density at sill depth outside the fjord is the same as that of the deep waters within the fjord which suggests that water entering the fjord over the sill controls the bottom water salinity of the fjord's outer and middle basins (Strøm, 1936; Pickard, 1961; 1963b; Herlinveaux, 1962). The temperature and salinity conditions observed in this part of Bolstadfjord by Strøm (1936) are plotted in Fig. 3.10 along with

those observed in 1971 at Bo 2. The most important point to be noted from the comparison is that the bottom waters remain constant in their salinity. Although it was noted above that a compensating inflow over the sill appeared to be absent in 1971, it may nevertheless be concluded that the salt water entrained by the surface outflow must be compensated over a period of time in order to maintain the constancy of bottom water salinity (see Fig. 3.2c).

A sub-surface O_2 maximum occurs within the fresh water layer at Bo 1 and Bo 2 (Figs. 3.9 and 3.10). This feature differs from the maxima found in the other fjords to the extent that it occurs above the halocline and can be attributed to the presence of a fresh water flora in Bolstadfjord (p. 33). Dissolved O_2 concentrations decrease with depth from these well-oxygenated, fresh waters to the saline waters at 30m (3.6 ml/l O_2 or <50% saturation). A much smaller decrease in O_2 is observed at Bo 4 (1972) between 20m and 30m (Fig. 3.11) corresponding to the zone of the temperature minimum described above. Unlike surface waters, variations in the dissolved O_2 content of the deep waters (>30m) appear unrelated to changes in temperature and salinity. A small maximum occurs at 40m in the profile at Bo 2 (1971) below which O_2 decreases gradually to 70m and then more slowly to the bottom where the water contains only 0.7 ml/l O_2. In contrast, O_2 decreases rapidly with depth below 40m at Bo 1 (1971) and is absent below ~55m. Although the O_2 concentration at 30m within the inner basin in 1972 (Bo 4) was considerably greater than in the previous year (Bo 1), similar concentrations existed at 40m on both occasions. Unfortunately O_2 was not measured below 40m

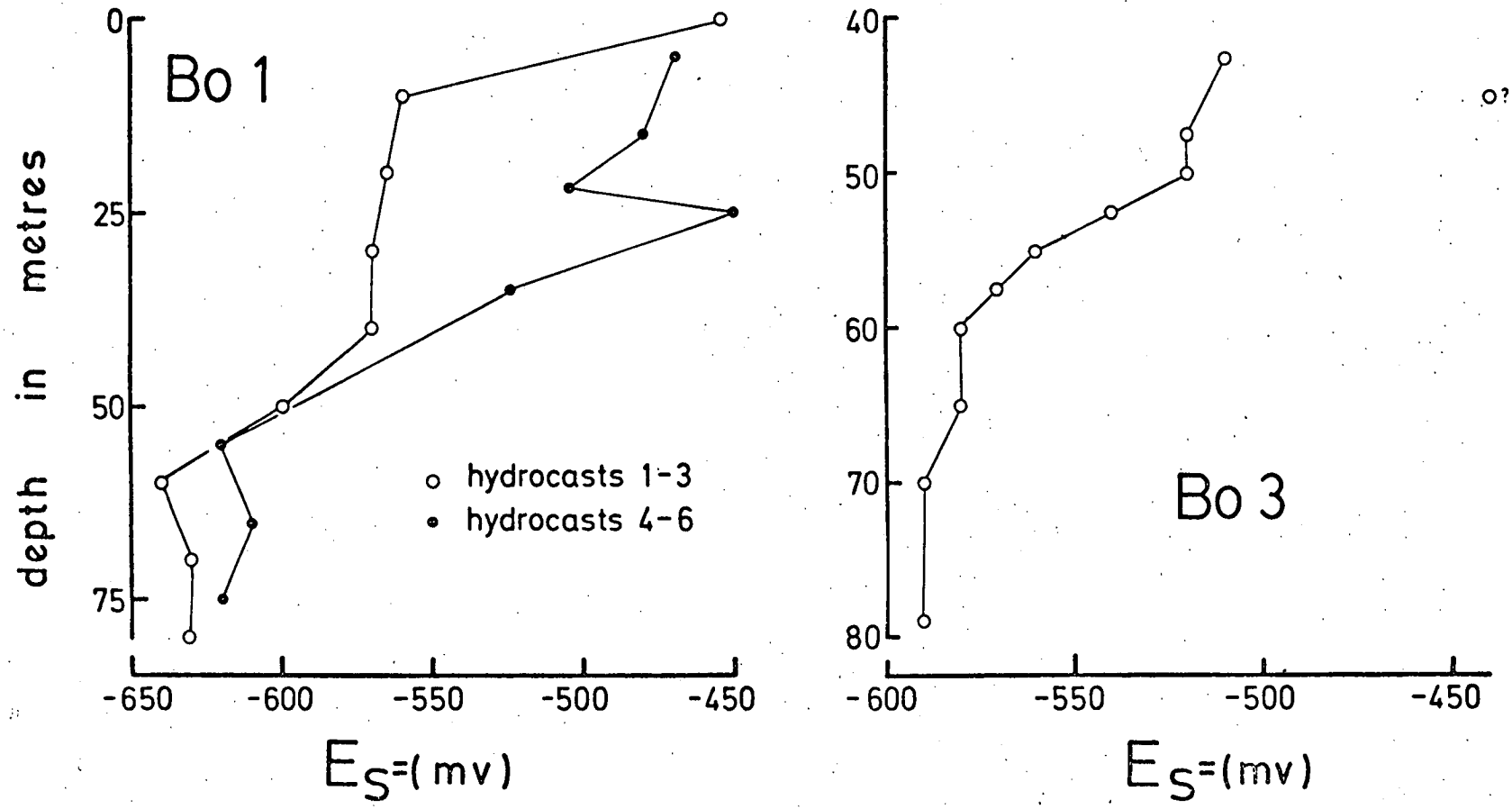
in 1972 at Bo 4 but its decrease with depth must have been pronounced as dissolved H_2S was detected at 51m. Therefore the depth of the O_2-H_2S boundary in the inner basin appears to have been relatively unaffected by the hydrographic changes in the overlying waters between 1971 and 1972.

Some indication of the H_2S concentrations was gained from variations in response of a silver-silver sulphide electrode (Berner, 1963; see Appendix B). Profiles of $E_{S=}$ at stations Bo 1 and Bo 3 (Fig. 3.12) show that there is a marked increase in electrode response between ~45m and 60m. In contrast to observations in the anoxic waters, the $E_{S=}$ values in oxic waters are unreliable as the electrode responds to other half-cell reactions (Whitfield, 1971). In addition, fluctuations of electrode response in samples from different hydrocasts in the anoxic waters (Fig. 3.12) indicate that the electrode was affected by hysteresis and/or 'poisoning'. Hence the $E_{S=}$ values provide at best an indication of the trend in sulphide activity within these waters. To obtain an accurate measurement of the total concentration of dissolved sulphide species, a colorimetric method of analysis was employed in 1972 (Appendix B). The data obtained by this method indicate a linear increase in H_2S content with depth between ~51m and at least 75m (Fig. 3.11).

Dissolved phosphate and silicate were also measured within the inner basin of Bolstadfjord in 1972 (Appendix B). At Bo 4 (Fig. 3.11), silicate and phosphate concentrations increase slowly with depth from the surface to the O_2-H_2S boundary and then more rapidly to 67.5m and 62.5m respectively. Below this, the rate of phosphate increase with

Fig. 3.12

Profiles of potentials measured using a silver-silver sulphide electrode.



depth is less while silicate appears to decrease fractionally although within the limits of precision is constant. The phosphate and silicate distributions at Bo 6 are similar. However, they are different at Bo 5 (Fig. 3.13) in that the marked increase in gradients, which coincides with the O_2-H_2S boundary at Bo 4 and Bo 6, occurs at ~70m thus implying that the O_2-H_2S boundary also occurs at this depth. This confuses what otherwise appears to be a simple explanation of the depth at which the O_2-H_2S boundary is found. That is, the upper boundary of the anoxic zone is maintained at ~51-55m by water circulating over the innermost sill (~52m according to Strøm, 1936; see Fig. 2.5) from the middle basin of the fjord. Unfortunately it was not possible to explain this anomaly as it was not realised until sampling had been completed.

The dissolved sulphide and nutrient data for stations Bo 4 and Bo 6 indicate that the deep waters of the inner basin are vertically stratified except possibly within the bottom ~15m. In 1971, the density gradients[3] between 30m and 70m at stations Bo 1 and Bo 2 were 2.1×10^{-5} m^{-1} and 2.9×10^{-5} m^{-1} and suggest that vertical mixing was slightly better at Bo 1 (see also salinity gradients described above). This is surprising with the knowledge that only the inner basin is anoxic. Several possible explanations can be given to account for this trend. Firstly, the proximity of the inner basin to the River Vosso and hence to a greater supply of detrital organic

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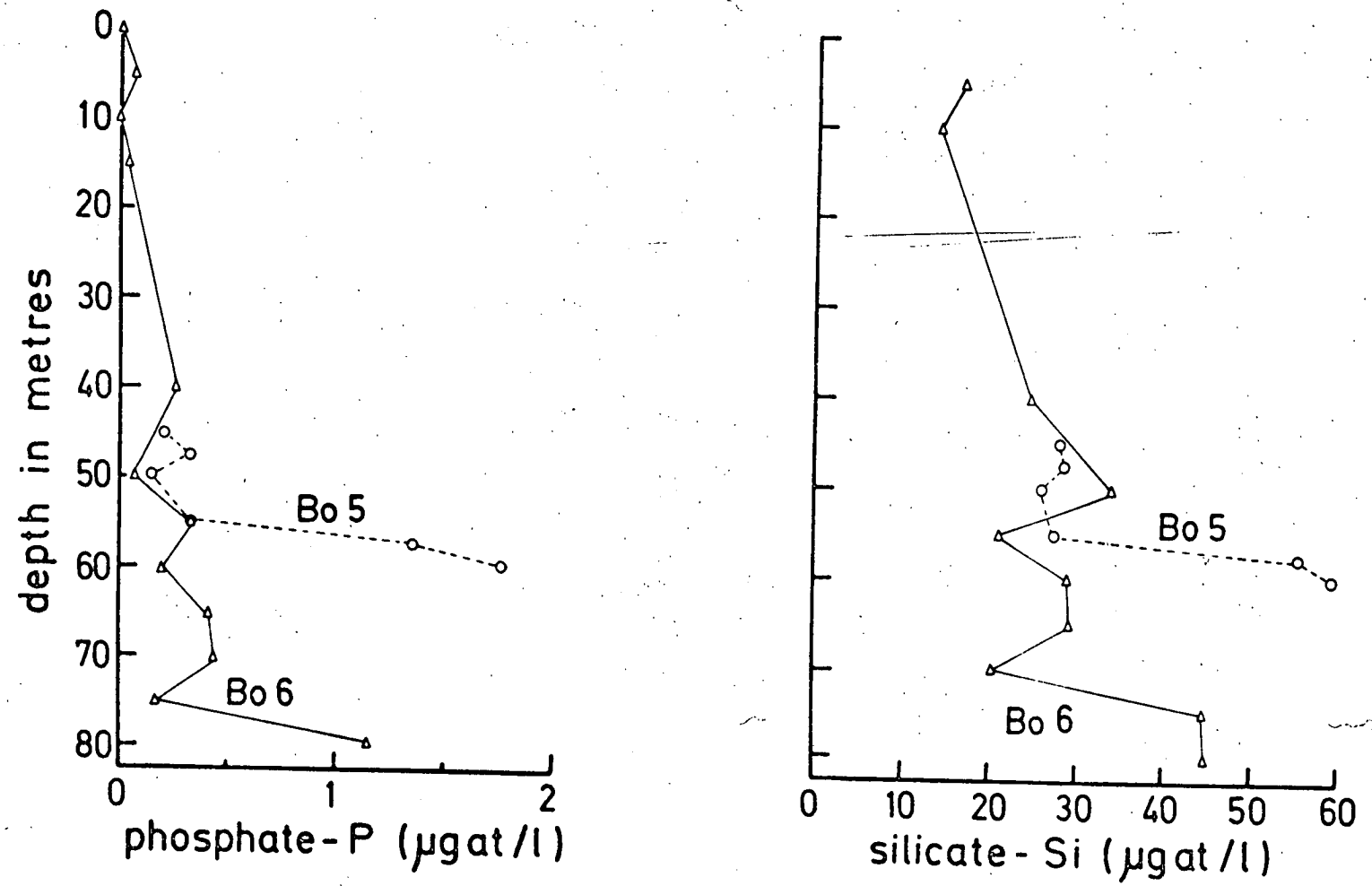
3 Density gradients expressed as 10^{-3}. $\frac{\Delta \sigma t}{\Delta z}$ m^{-1} where z is the depth. After Richards, 1965.

Fig. 3.13



Dissolved silicate-Si and phosphate-P profiles at Bo 5 and Bo 6, Bolstadfjord

matter may cause a greater consumption of O_2 in its deep waters. Alternatively, the decrease in salinity and O_2 gradients below 70m at Bo 2 may be the result of some kind of circulation (c.f. Molviksfjord and Mofjord) which supplies O_2 to the deep waters of the middle basin. The trend may also possibly be due to the fact that the deep waters of the outer and middle basins are completely renewed more regularly than are those of the inner basin.

3.8 Cause of Anoxicity

As stated above, the depletion of O_2 in the deep waters is essentially due to its consumption through the oxidation of organic matter, and to its limited supply which results from a lack of circulation. Circulatory processes are in turn affected by several independent factors such as the relative depths of basin and sill, the density of the water outside the basin at sill depth, tidal characteristics, the amount of runoff, and general meteorological conditions. Richards and Vaccaro (1956) and Richards (1965) have proposed that a critical value for the density gradient near sill depth must be present before anoxic conditions may develop. They consider 1×10^{-5} m^{-1} to be this critical value. Compared to values for several anoxic and poorly oxygenated basins, Mofjord, Molviksfjord and the outer basins of Bolstadfjord (Table 3.2) all have density gradients at sill depth far in excess of this 'critical' value and yet are oxic. This demonstrates that although an empirically derived, minimum density gradient may be obtained if a sufficient number of basins are studied, it is meaningless in terms of predicting whether the basin will develop

TABLE 3.2

Approximate stability across the sills of some basins and fjords. After Richards (1965)

BASIN	$\Delta\sigma_t/\Delta z \times 10^{-3}\ m^{-1}$	
Gulf of Mexico	2.0×10^{-6}	
Catalina Basin	3.1×10^{-6}	
Santa Barbara Basin	4.4×10^{-6}	Oxic
Santa Monica Basin	8.8×10^{-6}	
Kaoe Bay	2.4×10^{-5}	
Cariaco Trench	3.2×10^{-5}	
Gulf of Cariaco	3.5×10^{-5}	Anoxic
Saanich Inlet	1.5×10^{-5}	
Black Sea	3.0×10^{-4}	

Approximate stability at or below sill depth in Mofjord and Bolstadfjord

Mofjord: (sill depth = ~3m)	
0- 5m	2.8×10^{-3}
5-25m	4.7×10^{-4}
Bolstadfjord: (sill depth = ~2m)	
12-25m	Estimated at $1\text{-}2 \times 10^{-3}$

anoxic conditions. The same is true of the other factors affecting circulation if used in an attempt to characterise the development of anoxicity.

CHAPTER 4

HYDROCHEMISTRY

4.1 Dissolved O_2, H_2S, Phosphate-P, Silicate-Si, and Titration Alkalinity within the Inner Basin of Bolstadfjord.

The profiles of dissolved O_2, H_2S, phosphate-P and silicate-Si at Bo 4, Bo 5 and Bo 6 were described in section 3.7. Titration alkalinity[1] (determined electrochemically, see Appendix B) increases with depth throughout the water column at station Bo 4 (Fig. 4.1). There are marked increases in the titration alkalinity both across the halocline and at the O_2-H_2S boundary but below 60m its increase with depth is very slight. The specific alkalinity[2] of the near-surface, low salinity waters falls below the range of values reported for normal sea water (Table 4.1). This is probably due to the relatively low concentrations of bicarbonate and carbonate ions that exist at such low pH values (Skirrow, 1965) as those observed in the near-surface waters (p. 30). In contrast, the specific alkalinity of waters below 49m is above the range for normal sea water reaching a maximum of 0.191 which is similar to the highest value measured in the anoxic waters of Lake Nitinat (Table 4.1). These high values are attributed mainly to an increase in carbonate alkalinity (resulting from the oxidation of organic matter) but to some extent are due to

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1 Titration alkalinity is the sum of the analytical concentrations of the anions of carbonic and weaker acids which in normal sea water is equivalent to:- $[HCO_3^-] + 2[CO_3^{2-}] + [H_2BO_3^-] + [OH^-] - [H^+]$

2 Specific alkalinity = $\frac{\text{titration alkalinity} \times 10^3}{\text{chlorinity}}$

Fig. 4.1

Titration alkalinity profile at Bo 4

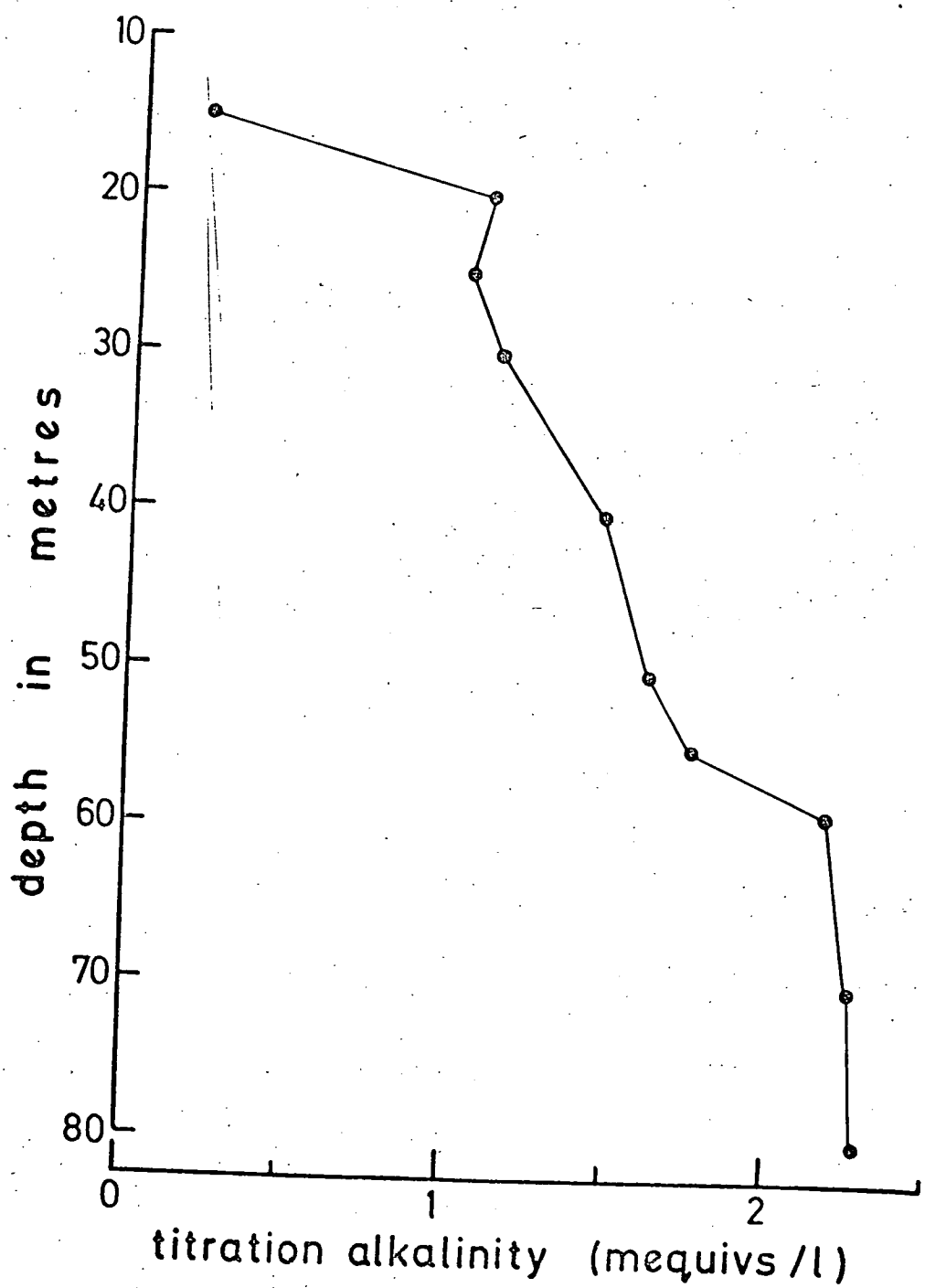


TABLE 4.1

Values of specific alkalinity at Bo 4

Depth (m)	Titration alkalinity (m equivs./l)	Specific alkalinity
15	0.194	0.108
20	1.083	0.139
25	1.031	0.115
30	1.136	0.120
40	1.452	0.125
49	1.594	0.136
55	1.757	0.149
59	2.158	0.181
70	2.245	0.189
75	2.270	0.191
Lake Nitinat (maximum value) - (Richards et al., 1965)		0.200
Normal sea water - (Skirrow, 1965)		0.119-0.130

relatively high concentrations of anionic species of sulphide-S, phosphate-P, and silicate-Si. The maximum concentrations of these three are compared with those found in other anoxic basins in Table 4.2.

There are two possible modes of origin of dissolved H_2S but both are related to the breakdown of organic matter. One is by its putrefaction particularly of proteinous material (Kriss, 1963). The other is one of bacterial sulphate reduction which Kaplan et al. (1963) and Deuser (1970) have shown to be the dominant process. The linear increase of dissolved H_2S with depth in the anoxic zone at Bo 4 (p. 21) may suggest that the gas originates from the sediments and is diffusing into the water column, although consumption of H_2S through its oxidation at the O_2-H_2S boundary could produce a similar profile. Kriss (1963) has shown that bacterial levels in anoxic, surface sediments of the Black Sea far exceed those in the overlying water column and therefore it seems reasonable to expect that the relative rates of sulphate reduction are similarly distributed. The author knows of no study of an anoxic marine basin where dissolved H_2S has been measured contemporaneously in both the pore waters and anoxic bottom waters. However reported H_2S concentrations in pore waters of Saanich Inlet sediments (maximum 5300μM/l) (Nissenbaum et al., 1972) far exceed those in the overlying anoxic waters (~20μM/l) (Richards, 1965). This supports the view that the upward flux of dissolved H_2S from anoxic sediments into anoxic bottom waters is the main source of the latter's H_2S content although Sorokin (1964) considers that sulphate reduction can also take place in the water column.

TABLE 4.2

Maximum concentrations of dissolved H_2S, phosphate-P, silicate-Si and titration alkalinity found in various anoxic basins

Locality and reference	H_2S (µg at./l)	phosphate-P (µg at./l)	silicate-Si (µg at./l)	Titration alkalinity (m equivs./l)
Inner basin of Bolstadfjord (this study)	193	2.88	62.60	2.27
Black Sea (Brewer, 1971)	601	9.92	227.00	4.47
Framvaren, a Norwegian fjord (Piper, 1971)	~935	~113.00	-	-
Cariaco Trench (Richards et al., 1956; Fanning and Pilson, 1972)	30	2.80	~70.00	-
Lake Nitinat, B.C. (Richards et al., 1965)	~340	~12.50	~180.00	-

The high phosphate-P and silicate-Si concentrations observed in the anoxic waters are the result of decomposition of organic material although, unlike H_2S and carbonate alkalinity, their origin is not directly linked to redox processes. Redfield et al. (1963), Richards (1965) and others have applied a stoichiometric model to organic matter breakdown using the average composition of marine plankton (atomic C:N:P = 106:16:1). The successive steps in its breakdown (i.e. by oxygen, denitrification and sulphate reduction) may be represented as follows (Richards, 1965):-

$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 138\ O_2 = 106\ CO_2 + 122\ H_2O + 16\ HNO_3 + H_3PO_4 \quad ..A$$

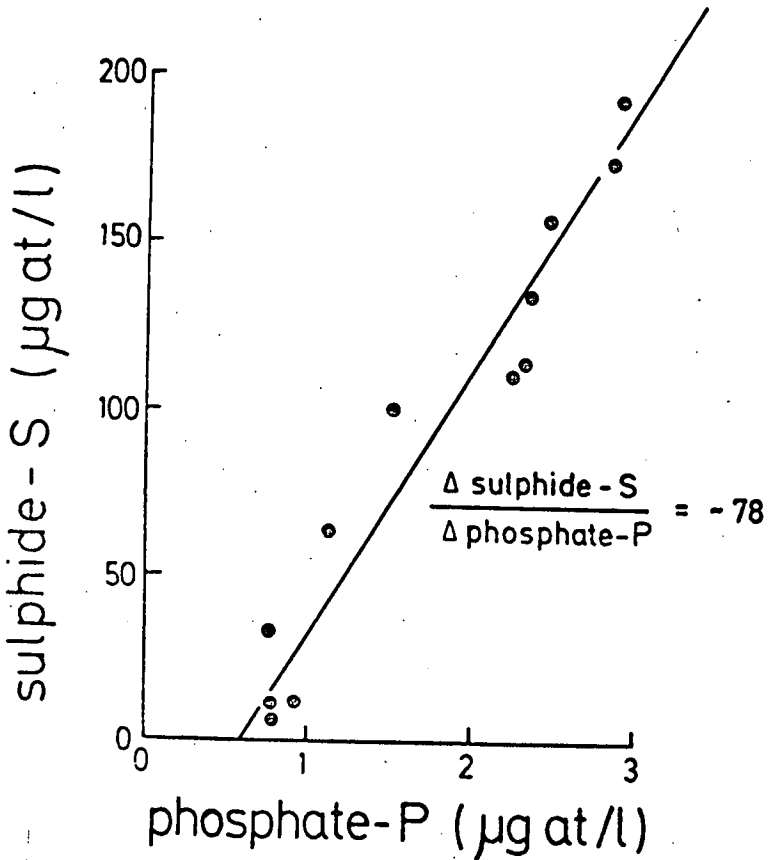
$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 84.8\ HNO_3 = 106\ CO_2 + 42.4\ N_2 + 148.4\ H_2O + 16\ NH_3 + H_3PO_4 \quad ..B$$

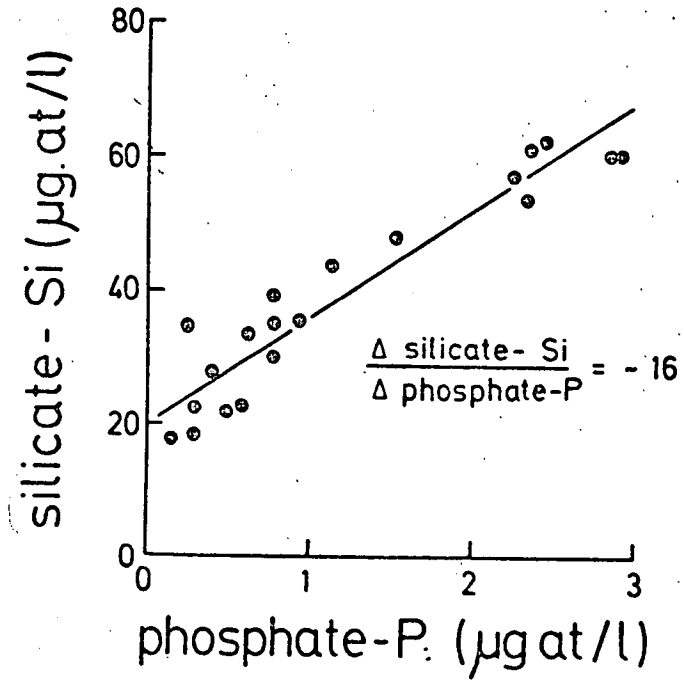
$$(CH_2O)_{106}(NH_3)_{16}H_3PO_4 + 53\ SO_4^{2-} = 106\ CO_2 + 53\ S^{2-} + 16\ NH_3 + 106\ H_2O + H_3PO_4 \quad ..C$$

Thus in a closed system initially saturated with O_2, it is theoretically possible to predict the quantitative relationships between the products of organic decomposition. The observed value of Δ sulphide-S/Δ phosphate-P in the anoxic waters at Bo 4 is ~78 (Fig. 4.2) which is considerably higher than that predicted (53) by equation C above. This may partly be a reflection of the abundance of terrestrial plant debris in the fjord sediments (p. 45) since such material has a much lower phosphorus content (atomic C:P ~500 according to the data of Bowen, 1966). No covariance between the oxygen consumed during oxidation by free O_2 and the phosphate-P concentrations exists in the oxic waters below 30m although there should be a $\Delta O/\Delta P$ value of 276 according to equation A above. The ratios (~500-1400) are invariably

Fig. 4.2

Dissolved sulphide-phosphate and silicate-phosphate relationships at Bo 4





far in excess of this value, perhaps in part due to the abundance of terrestrial organic matter.

The observed Δ silicate-Si/Δ phosphate-P value is 16 in the anoxic waters at Bo 4 (Fig. 4.2). Grill and Richards (1964) observed experimentally the concurrent release of silicate-Si and phosphate-P from phytoplankton in the ratio 16:1 which is also close to the value suggested by Richards (1958) from observations made in the North Atlantic Ocean and Caribbean Sea. The similarity between these and the observed values suggest that most of the phosphate-P present in the anoxic zone at Bo 4 is derived from plankton as opposed to terrestrial matter. This does not preclude the possible significance of terrestrial organic matter in consuming oxygen (see above) as the amount of phosphorus thus released would be relatively small.

In conclusion, the relationships between dissolved H_2S, phosphate-P and silicate-Si suggest a common origin, organic matter breakdown. The observed concentrations however, are not those predicted by the simple stoichiometric model which assumes that oxidation has proceeded in a closed system and that the initial material has a uniform composition similar to that of marine plankton. The real reasons for the disparities may not be as simple as was suggested above. For instance, the ratios between the initial organic decomposition products may not reflect those in the original organic detritus, and the decomposition products, if derived from the sediments, may not occur within the water column in the ratios that existed immediately after decomposition due to their reactions with solid phases in the sediment (i.e. sulphide precipitation, carbonate

precipitation) (Sholkovitz, 1973).

4.2 Eh

Eh (and pH) was measured (Appendix B) at all stations occupied in 1971. Eh electrode response varies little (+350 to +475 mV) in the water column at stations No 49 and Bo 2 (Fig. 4.3). However, there is a much greater variation (-70 to +550 mV) within the inner basin of Bolstadfjord (Bo 1 and Bo 3; see Fig. 4.3) where most of this change occurs across the O_2-H_2S boundary as in the Black Sea (Skopintsev, 1957).

Eh is ideally a measure of the oxidising or reducing potential of a system but its measurement is problematical both in regard to the practical difficulties of electrode performance and to the thermodynamic interpretation of the results (Morris and Stumm, 1967). For instance somewhat erratic electrode response is demonstrated by the data for hydrocasts 1-3 and 4-6 at station Bo 1 (Fig. 4.3) and it is known that not all redox equilibria behave reversibly at the electrode surface.

Table 4.3 shows observed pE[3] values at Bo 1 and those calculated using the oxygen-hydrogen couple, which defines pE in oxygenated waters (Sillén, 1961), and the sulphide-sulphate couple, which defines pE in the anoxic zone. The calculated values deviate considerably from those observed in all instances which may partly be the result of the low exchange currents for the above reactions at a platinum electrode (Berner, 1971). Measured pE (Eh) in sulphide-rich sediment pore waters has been attributed to the following half cell reaction (Berner, 1963):-

$$S^{2-} = S^0 (s) + 2e .$$

---

3 $pE = \frac{F}{2.3RT} \cdot Eh$ where F = the Faraday constant, R = the gas constant and T = absolute temperature, Kelvin.

Fig. 4.3

Eh and pH profiles at stations occupied in 1971.

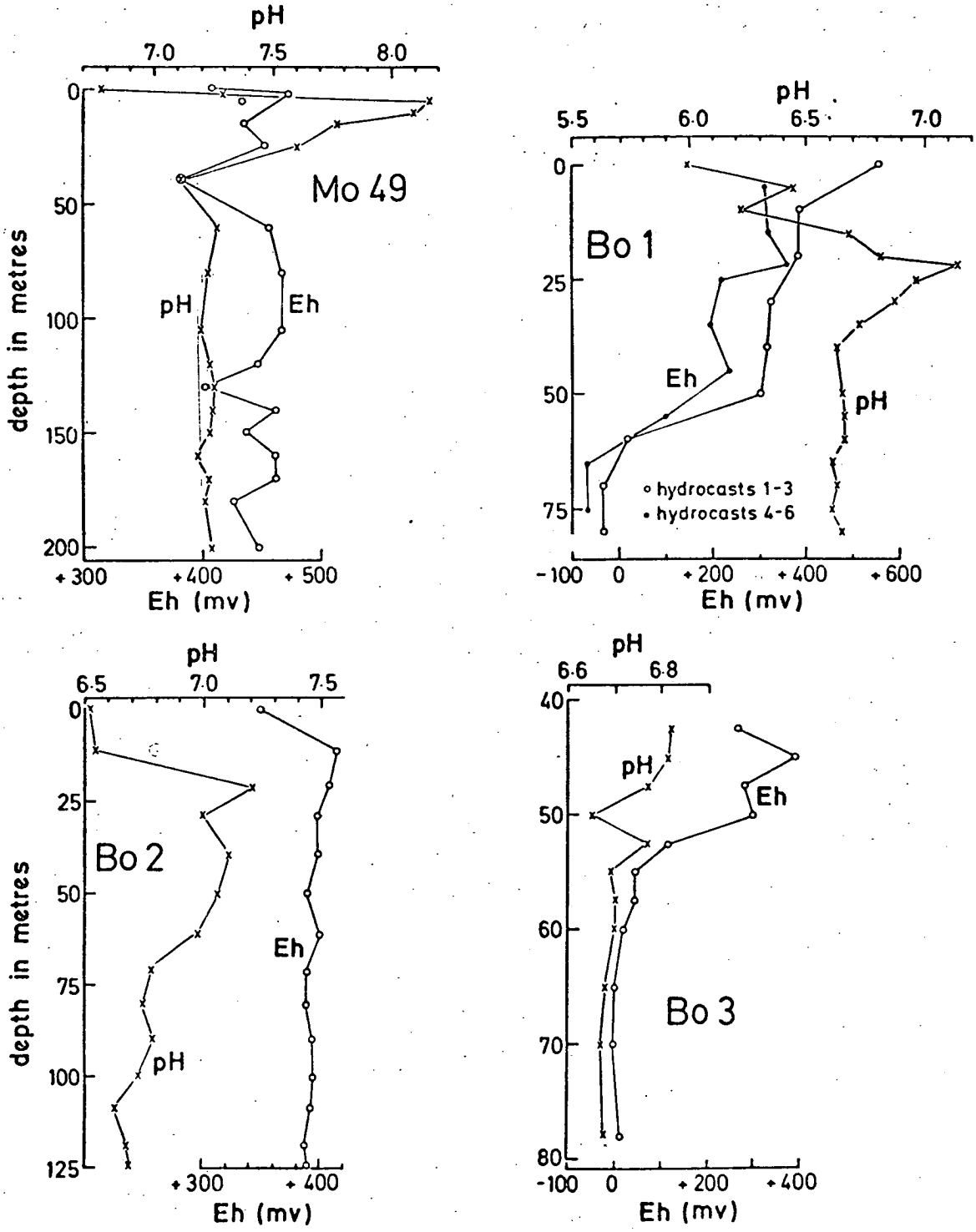


TABLE 4.3

Calculated pE values
for various reactions at Bo 1

Depth (m)	Observed pH	$-\log[H_2S]$	pO_2	Observed pE	A	B	C
0	5.98		0.179	+9.70	+14.6		
10	6.21		0.178	+6.74	+14.4		
20	6.81		0.176	+6.77	+13.8		
30	6.86		0.084	+5.85	+13.6		
40	6.62		0.094	+5.78	+13.9		
50	6.65		0.017	+5.42	+13.6		
55	6.66	4.65	0.005	+1.78	+13.5	-2.36	-1.44
60	6.66	4.17		+0.33		-2.42	-1.69
65	6.61	4.12		-1.22		-2.35	-1.66
70	6.63	4.04		-0.67		-2.39	-1.72
75	6.61	3.93		-1.22		-2.38	-1.76
80	6.65	3.88		-0.69		-2.43	-1.82

A pE calculated from $\frac{1}{4}O_2(g) + H^+(w) + e = \frac{1}{2}H_2O \quad pE^o = +20.75$

B pE calculated from $\frac{1}{8}SO_4^{2-} + \frac{5}{4}H^+(w) + e = \frac{1}{8}H_2S(g) + \frac{1}{2}H_2O$
$pE^o = +5.75$

C pE calculated from $\frac{1}{2}S(s) + H^+(w) + e = \frac{1}{2}H_2S(g) \quad pE^o = +2.89$

A, B, and C - after Stumm and Morgan (1970)

$-\log[H_2S]$ = negative logarithm of $H_2S(g)$ concentration assuming total $H_2S = [H_2S] + [HS^-]$ and $H_2S = HS^- + H^+ \quad pK_1 = 7$

SO_4^{2-} activity taken as $10^{-2.9}$

There is some evidence (p. 41) that elemental S, which must be present if this couple is responsible for the pE measured at Bo 1, exists in the anoxic waters. As H_2S is the dominant sulphide species at the in situ pH (6.6) (assuming ionisation constants for H_2S of $pK_1 = 7$ and $pK_2 = 12.9$; after Krauskopf, 1967), the equivalent H_2S-S^0 couple is used to calculate pE values (Table 4.3). These also differ from the observed pE values but are closer to them than the values calculated from the sulphide-sulphate couple. Other possible pE controlling reactions occurring in the water column at Bo 1 are discussed on p. 83 .

4.3 pH

At station No 49, there is a very low surface pH, a subsurface maximum, and an intermediate and constant pH in the well-mixed waters below 45m (Fig. 4.3). The profiles at Bo 1 and Bo 2 are similar except that the pH in the latter profile decreases gradually with depth in the deep waters (Fig. 4.3). The range of observed pH values (6.0-8.2) is greater than that for normal sea water (7.8-8.3) (Skirrow, 1965). The low pH of the surface waters may be attributed to the runoff of poorly buffered, slightly acidic waters. The coincidence of the highest pH values with the base of the halocline at all three stations rather than with the observed O_2 maxima (see Chapter 3) suggests that the pH maxima result from normal sea water being sandwiched between low pH waters. The origin of the low pH waters in the deeper parts of Bolstadfjord and Mofjord is probably related to the increased concentrations of anionic decomposition products of organic matter (see p. 25).

CHAPTER 5

SUSPENDED PARTICULATE MATTER

5.1 Introduction

Suspended particulate matter (>0.45μ) was collected in 1970, 1971 and 1972 at all the stations shown in Fig. 3.1 except Mo 34 and Bo 6. All samples were analysed for Ca, K, Fe, Ti, Si, Al, Mg, P and Mn by X-ray fluorescence spectrometry. X-ray diffraction of the 1970 samples showed that considerable amounts of salt remained on the filter papers despite thorough washing. Therefore Cl (and S) was determined in samples collected during 1971 and 1972 in order that Ca, K, Mg and S concentrations could be 'salt corrected' (Appendix D). Scanning electron microscopy (S.E.M.) and X-ray diffraction were used to identify the major constituents of the particulate matter.

Total suspended matter was determined gravimetrically in 1971 and an estimate of the inorganic matter content was obtained from the sum of elements expressed as oxides; Fe being expressed as Fe_2O_3, Mn as MnO_2, and S as S^0. The concentration of elements expressed in this manner should be equivalent to more than 90% by weight of the inorganic constituents of an average argillaceous sediment (c.f. Wedepohl, 1968).

More detailed descriptions of the sampling and analytical methods are included in Appendices A and C respectively and a complete set of tabulated analytical data in Appendix D.

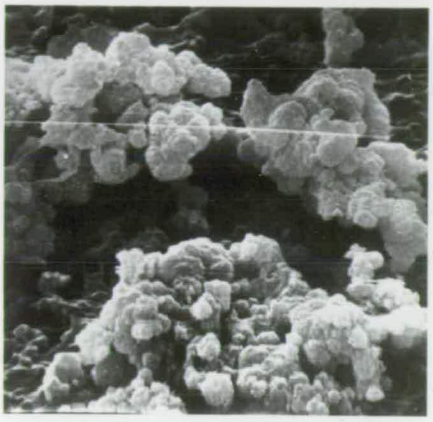
5.2 Major Constituents

Most samples when diffracted show a sharp and symmetrical peak at ~10Å which is attributed to micaceous material (illite). The characteristics of the reflection, which are its shape and sharpness, are similar to those in illite from the underlying sediments and indicate that it is well-crystallised (p. 47). A smaller peak at 3.34Å probably represents quartz. The sample collected from a depth of 20m at Bo 1 is unique in that the quartz peak is larger than the 10Å peak and in that two additional reflections exist at 9.4Å and 3.1Å which have not been identified. In the underlying sediments, the quartz and feldspar reflections are invariably more intense than the 10Å peak. The general dominance of the 10Å reflection in the suspended particulate matter may indicate that there is a relative enrichment of micas within the water column although the way in which particulate matter is sampled results in the orientation of minerals, whereas the diffraction method for the underlying sediments involves the use of unorientated samples. The more rapid settling of quartz and feldspars relative to minerals of a platy habit could account for the enrichment as suggested by Rodolfo (1964) to explain a similar feature observed in waters off California. Other minerals, present in considerable concentrations within the underlying sediments (e.g. chlorite and amphibole), are not found in the suspended particulate matter perhaps due to the insensitivity of the analysis.

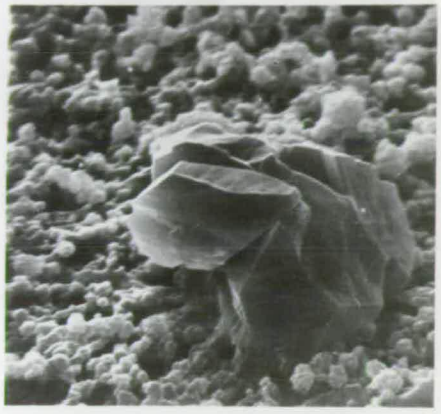
The S.E.M. photographs show that the suspended particulate matter is variable in grain size, mainly in the range <1–$50\ \mu$, but is predominantly at the fine end of this range (Figs. 5.1 and 5.2).

FIG. 5.1 Photomicrographs of particulate matter

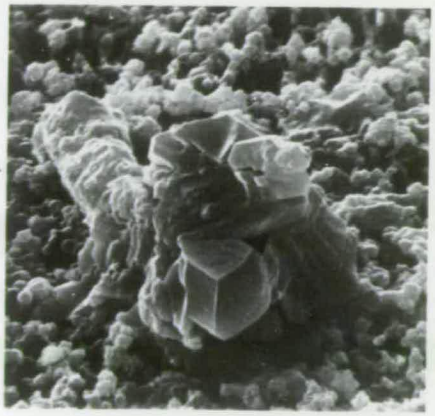
a) Mo 49, 210 m.
10 μ x 10 μ



b) Mo 49, 210 m.
20 μ x 20 μ



c) Mo 49, 210 m.
20 μ x 20 μ



d) Bo 1, 75 m.
100 μ x 100 μ

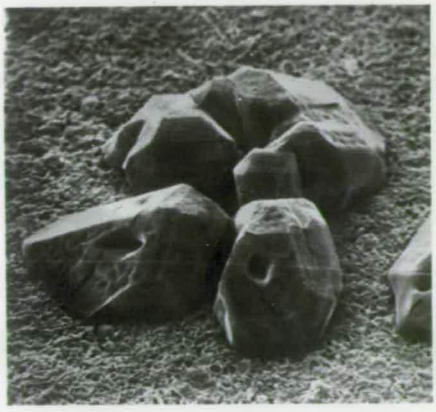
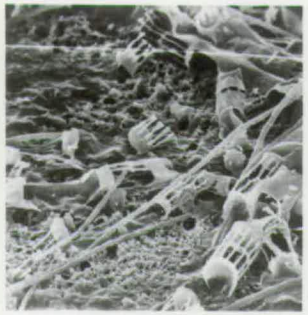


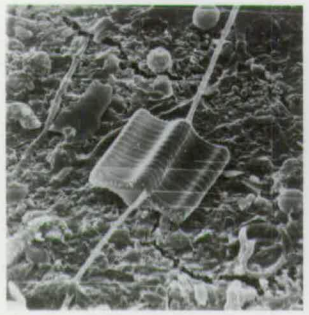
FIG. 5.2 Photomicrographs of particulate matter

a) Mo 49, 5 m.
50 μ x 50 μ

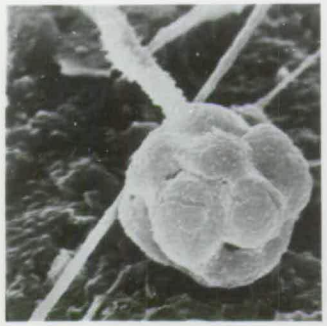


b) Mo 49, 5 m.
100 μ x 100 μ

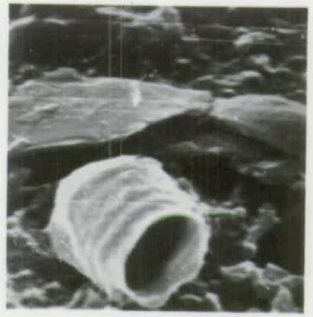
c) Bo 1, 20 m.
50 μ x 50 μ



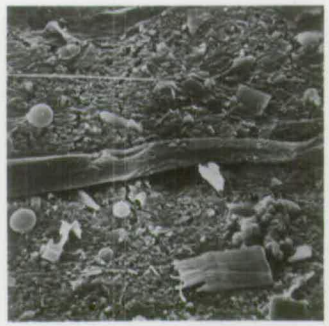
d) Bo 1, 20 m.
20 μ x 20 μ



e) Bo 1, 20 m.
10 μ x 10 μ



f) Bo 1, 20 m.
100 μ x 100 μ



As a comparison, d'Anglejan (1970) estimated that more than 90% of the suspended particles in the Gulf of St. Lawrence were >2μ in size. The S.E.M. photograph of the sample collected from 20m at Bo 1 shows a uniform film of material (Fig. 5.2c and f) that is probably due to orientated clay minerals. Much material of organic origin is evident in the S.E.M. photographs (Fig. 5.2), particularly diatom frustules in the near-surface waters. The remains of the marine diatom, Skeletonema costatum, is commonly seen in the particulate matter of Mofjord (Fig. 5.2a and b) whereas the fresh water species, Tabellaria flocculosa, occurs in the waters of Bolstadfjord (Fig. 5.2c). Although frustules of T. flocculosa may be introduced into the fjord via runoff, the total absence of S. costatum in the waters of Bolstadfjord suggests that a largely fresh water biota exists there probably due to the thick (~17m) low salinity surface layer of water. Other organisms, which have been tentatively identified, are the 'house' of the chrysophycean, Calycomonas c.f. fragilis (Fig. 5.2e), and a coccolithophorid (Fig. 5.2d).

5.3 Distribution of Suspended Particulate Matter

A comparison of the 1971 data for total and inorganic suspended particulate matter with that for other waters (Table 5.1) shows that the observed range overlaps with values reported for open ocean and near-shore waters. By difference, it is estimated that organic particulate matter comprises roughly 60-90% of the total particulate matter and varies between 0.12-0.62 mg/l. Similar values have been reported for near-shore waters (0.2-0.3 mg/l or 90-95% of the total suspensate) (Beer and Gorsline, 1971) and for waters of a glacial

TABLE 5.1

Suspended particulate matter (S.P.M.) concentrations (in mg/l)

Locality and reference	Total S.P.M.	Inorganic S.P.M.
Fjord water, Bergen area (this study, 1971 data)	0.15-1.49	0.03-0.59
English Channel (Armstrong, 1958)	-	0.16-1.20
Somes Sound, a Maine fjord (Folger et al., 1972)	0.6 -4.1	-
N.E. Atlantic Ocean (surface waters) (Copin-Montegut and Copin-Montegut, 1972)	0.03-0.23	-

estuary (0.035–0.65 mg/l) (Loder and Hood, 1972).

The main rivers entering Bolstadfjord and Mofjord, the Vosso and the Moelv respectively, generally have inorganic particulate loads similar to the surface fjord waters whereas total particulate and hence organic matter tends to be more concentrated in the surface fjord waters. There is a marked near-surface maximum of total particulate matter at several stations which is coincident with the pycnocline (Figs. 5.3 and 5.4). There are several possible contributary reasons for the maxima:-

a) the pycnocline acts as a physical barrier to settling (Jerlov, 1959; Postma, 1967; Beer and Gorsline, 1971).

b) the recycling of particulate matter by the surface circulation. For example Postma (1967) has suggested that within basins having an estuarine circulation, particulate matter penetrating the pycnocline may be transported towards the head of the basin by the compensating current and then returned to the surface outflow by entrainment.

c) the flocculation of clay minerals (Whitehouse et al., 1960; Postma, 1967).

d) <u>in situ</u> biological productivity.

The most important causes are probably a and d. Waters below the pycnocline and more than 20m above the surface of sedimentation generally contain small amounts of particulate matter whereas bottom waters sometimes contain high concentrations (e.g. Mo 23, Mo 49 and to some extent Bo 2 as shown in Figs. 5.3 and 5.4).

Fig. 5.3

Suspended particulate matter profiles.

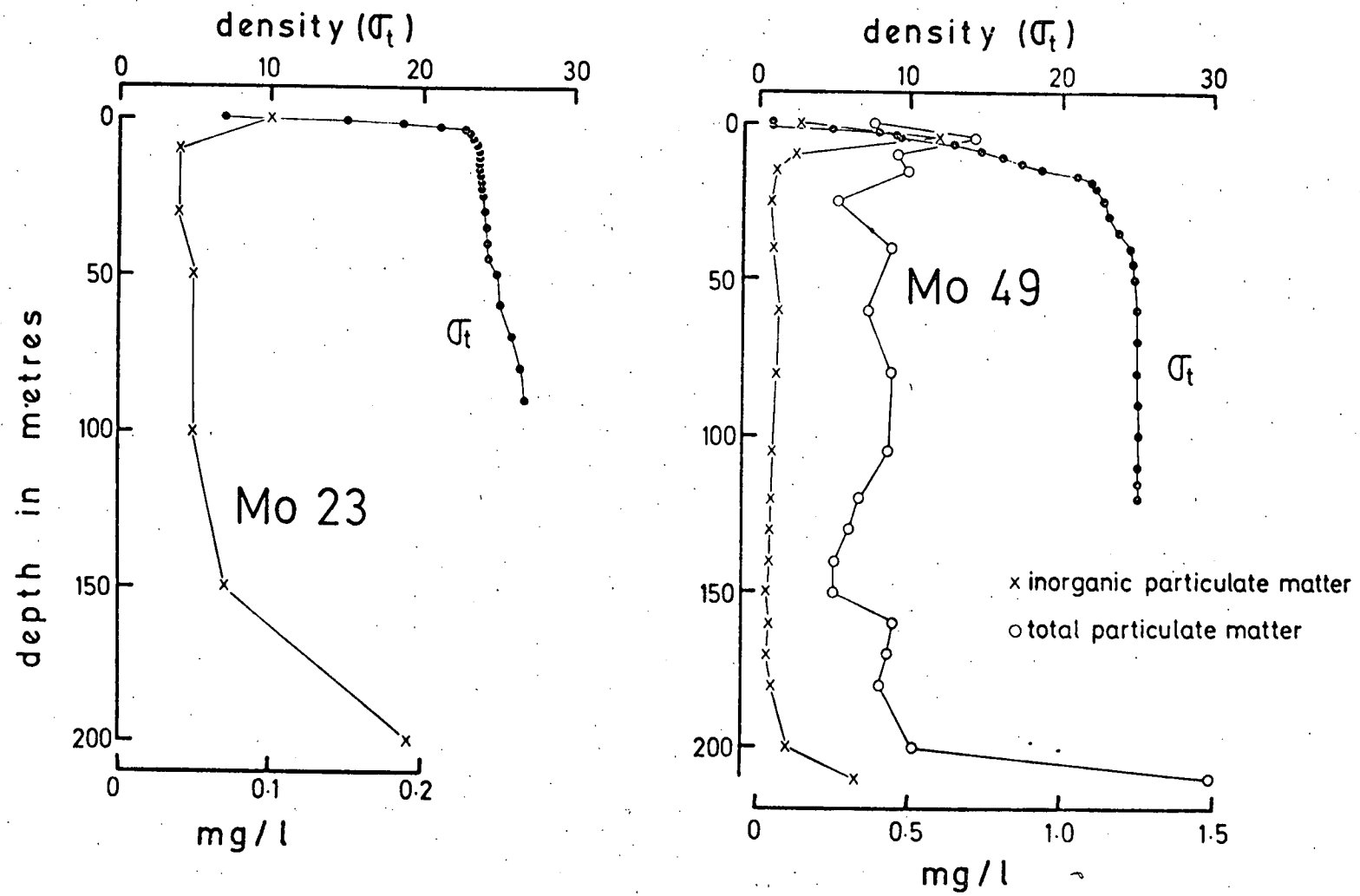
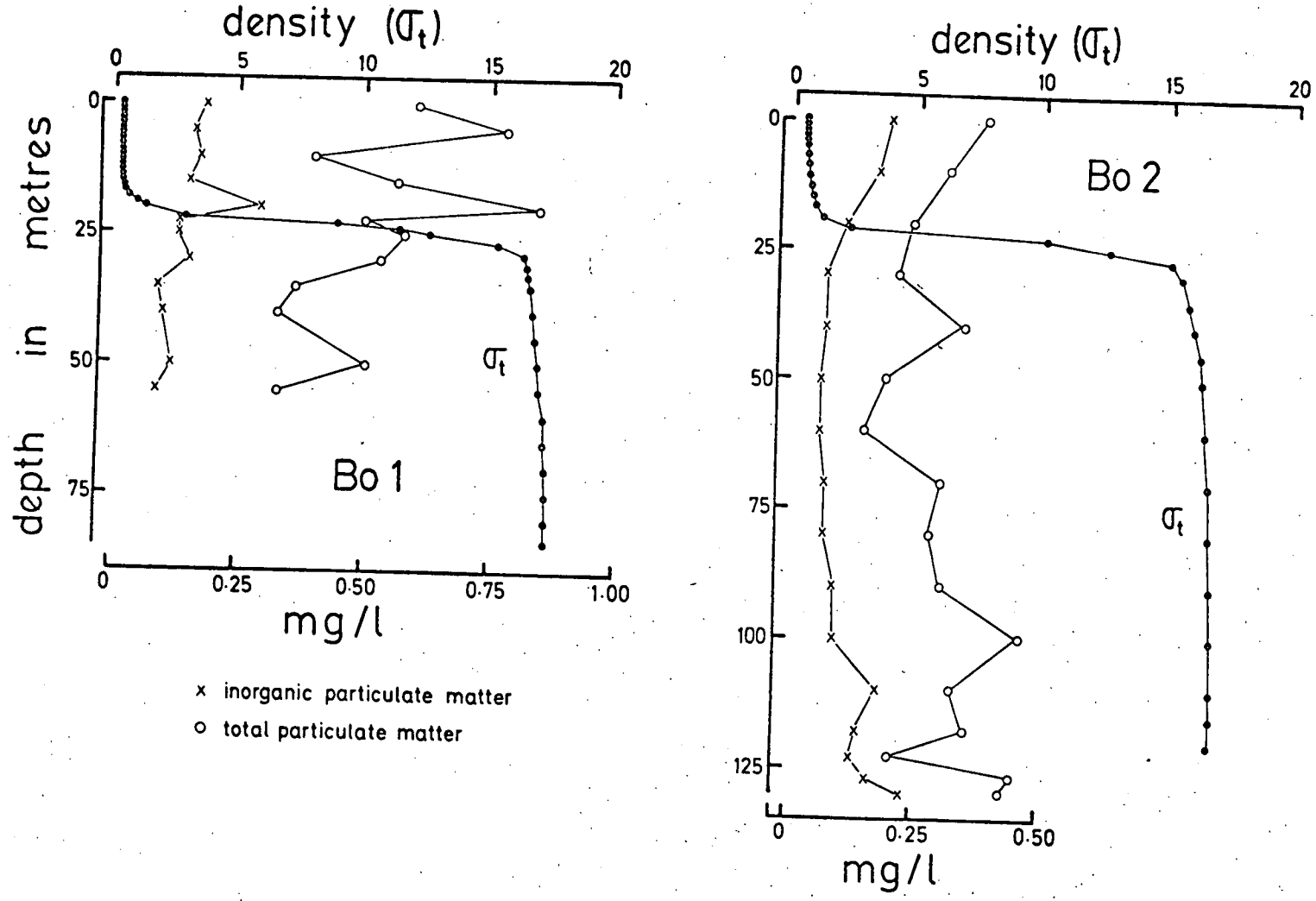


Fig. 5.4

Suspended particulate matter profiles.



5.4 Elements Predominantly Associated with Detrital Silicates

Particulate Al is predominantly held in detrital aluminium-silicate minerals and will be used as an indicator of their concentration (d'Anglejan, 1970; Spencer and Sachs, 1970; Price and Calvert, 1973). The range of particulate Al concentrations (Table 5.2) is similar to that reported for the Gulf of St. Lawrence (1-20 µg/l) by d'Anglejan (op. cit.) and for near-shore waters (0.4-70 µg/l) by Atkinson and Stefansson (1969). Table 5.2 shows the observed range of particulate Si, K, Mg, and Ti; all show some covariance with particulate Al concentrations (Fig. 5.5). K, Mg and Ti are also likely to be associated predominantly with aluminium silicates while Si is additionally held as quartz and diatom frustules. Four samples, collected in 1971 from the River Moelv and the surface 2m of water in Mofjord, are exceptional in that particulate Al is greatly enriched relative to particulate Si, K, Mg and Ti (Fig. 5.5 and Table 5.3). This excess particulate Al may be brought into the fjord as a hydrous oxide or hydroxide of aluminium; its absence below 2m in the fjord could be due either to its simultaneous removal via the surface outflow (p. 10) or to the increased solubility of aluminium at the higher pH (Stumm and Morgan, 1970) existing in the sub-surface waters (p. 30).

Figs. 5.7 and 5.8 show that particulate Al, Si, Ti, Mg and K are concentrated at the pycnocline at stations Mo 49 and Bo 1 respectively. Although surface concentrations of these five elements are similar in Bolstadfjord and Mofjord, the concentrations in the deeper waters (below the pycnocline) of Bolstadfjord are significantly

TABLE 5.2

Element concentrations
in suspended particulate matter (in µg/l)

Element	Range	Average
Al	<0.50- 24.49	8.00
Si	3.91-209.91	25.70
K	<0.50- 9.26	3.10
Mg	<0.01- 10.12	2.00
Ti	<0.03- 1.62	0.42
Ca	<0.08- 13.56	2.20
P	0.57- 13.12	3.20
S	1.35-2119	-

P values obtained from samples collected in 1970 and 1971 only.

TABLE 5.3

Element/Al and K/Mg ratios in particulate matter

Station and Date	Depth (m)	Si/Al	K/Al	Mg/Al	Ti/Al	Ca/Al	K/Mg
Mo 49	0	1.14	0.13	0.08	0.020	0.04	1.57
1971	0*	1.20	0.12	0.08	0.020	0.06	1.59
	2*	1.26	0.13	0.09	0.020	0.08	1.42
	5	10.78	0.48	0.30	0.074	0.38	1.60
	5*	6.22	0.37	0.25	0.057	0.20	1.50
	10	7.14	0.61	0.43	0.056	1.07	1.40
	10*	9.32	0.53	0.26	0.068	0.57	2.05
	15	5.75	0.69	0.41	0.060	1.01	1.67
	25	7.18	1.37	0.66	0.052	1.25	2.10
	40	5.84	0.70	0.24	0.048	0.97	2.98
	60	5.01	0.59	0.69	0.100	0.56	0.85
	80	4.48	0.49	0.96	0.091	0.95	0.51
	105	3.61	0.51	0.24	0.083	0.94	2.16
	120	4.77	1.28	0.41	0.085	1.32	3.08
	130	4.03	0.66	0.25	0.091	0.88	2.64
	140	4.02	0.80	0.20	0.075	0.90	3.92
	150	4.15	1.02	0.21	0.102	1.02	4.76
	160	4.30	0.58	0.28	0.072	0.92	2.05
	170	2.62	1.33	0.01	0.040	2.18	-
	180	4.00	0.65	0.41	0.088	0.92	1.57
	200	3.56	0.73	0.39	0.083	1.84	1.87
	210	2.38	2.13	1.65	0.085	8.27	1.29
bottom sediments at Mo 49		3.82	0.35	0.17	0.065	0.36	2.02
River Moelv 1971		1.48	0.14	0.08	0.032	0.19	1.90
River Beitleelv 1971		3.26	0.29	0.06	0.038	0.03	5.31
Mo 23+	0	5.50	0.51	0.36	0.071	0.28	1.40
1970	10	8.35	2.20	2.06	0.028	2.39	1.07
	30	5.32	1.23	1.03	0.040	1.07	1.20
	50	4.86	0.47	0.50	0.052	0.25	0.93
	100	5.10	1.01	0.78	0.042	0.95	1.30
	150	4.52	0.41	0.45	0.062	0.20	0.91
	200	4.46	0.50	-	0.063	0.86	-
bottom sediments at Mo 23		3.36	0.38	0.17	0.060	0.43	2.20
Average shale (Krauskopf, 1967)		2.98	0.29	0.17	0.056	0.31	2.20

* sampled by a second hydrocast in near-surface waters.

\+ not salt corrected

Table 5.3 continued

Station and Date	Depth (m)	Si/Al	K/Al	Mg/Al	Ti/Al	Ca/Al	K/Mg
Bo 1	0	2.34	0.21	0.13	0.036	0.05	1.60
1971	5	2.29	0.20	0.12	0.029	0.13	1.68
	10	2.34	0.27	0.15	0.036	0.14	1.77
	15	2.56	0.22	0.15	0.031	0.17	1.50
	20	2.96	0.26	0.40	0.065	0.20	0.66
	22.5	2.80	0.25	0.17	0.033	0.19	1.51
	25	2.91	0.27	0.19	0.035	0.20	1.46
	30	3.18	–	–	0.059	–	–
	35	2.72	0.30	0.18	0.031	0.17	1.69
	40	2.59	0.26	0.17	0.046	0.12	1.51
	50	2.35	0.36	0.19	0.035	0.28	1.86
	55	2.41	0.30	0.21	0.034	0.24	1.44
	60	2.69	0.35	0.26	0.039	0.15	1.33
	65	2.49	0.25	0.25	0.034	0.07	1.02
	70	2.38	0.31	0.14	0.037	0.08	2.18
	75	2.25	0.21	0.25	0.015	0.09	0.85
	80	2.45	0.27	0.14	0.043	–	2.01
bottom sediments at Bo 1		3.14	0.28	0.21	0.069	0.22	1.38
Bo 2	0	2.55	0.23	0.12	0.038	0.10	1.89
1971	10	2.43	0.21	0.11	0.028	0.03	1.90
	20	2.92	0.29	0.17	0.035	0.17	1.71
	30	2.99	0.37	0.14	0.038	0.22	2.67
	40	2.90	0.37	0.13	0.051	0.23	2.74
	50	2.73	0.33	0.14	0.032	0.19	2.34
	60	2.50	0.32	0.14	0.030	0.12	2.22
	70	2.37	0.32	0.17	0.030	0.15	1.93
	80	2.65	0.36	0.18	0.033	0.12	2.03
	90	2.60	0.47	0.20	0.036	0.25	2.41
	100	2.60	0.41	0.19	0.040	0.28	2.18
	110	2.65	0.49	0.30	0.040	0.62	1.62
	118	2.52	0.36	0.19	0.054	0.62	1.95
	123	2.55	0.52	0.32	0.037	0.69	1.63
	124	2.34	0.60	0.61	0.048	1.79	0.99
	127	2.67	0.59	0.33	0.040	0.91	1.78
	130	2.66	0.55	0.43	0.040	1.32	1.29
bottom sediments at Bo 2		3.16	0.28	0.17	0.063	0.24	1.54
Bo 3	42.5	2.35	0.30	0.15	0.034	0.14	2.01
1971	45	2.36	0.37	0.18	0.034	0.22	2.11
	47.5	2.49	0.34	0.20	0.060	0.33	1.71
	50	2.38	0.33	0.20	0.051	0.55	1.62
	52.5	2.65	0.33	0.25	0.095	0.34	1.34
	55	2.70	0.30	0.18	0.060	0.27	1.68
	57.5	2.47	0.38	0.23	0.048	0.22	1.63
	60	2.89	0.31	0.25	0.065	0.19	1.25
	65	2.62	0.33	0.21	0.058	0.64	1.59
	70	2.47	0.27	0.19	0.044	0.07	1.42
	78	2.57	0.35	0.21	0.046	0.20	1.69
River Vosso 1971		2.51	0.26	0.14	0.029	0.14	1.88

Table 5.3 continued

Station and Date	Depth (m)	Si/Al	K/Al	Mg/Al	Ti/Al	Ca/Al	K/Mg
Bo 5 1972	0	2.90	0.36	0.23	0.046	0.26	1.52
	5	2.70	0.31	0.23	0.072	0.21	1.33
	10	2.92	0.33	0.29	0.044	0.14	1.13
	15	2.85	0.20	0.21	0.053	0.17	0.98
	40	5.49	0.44	0.40	0.085	0.32	1.12
	45	4.08	0.28	0.26	0.063	0.20	1.06
	50	3.70	0.29	0.27	0.065	0.19	1.07
	55	3.88	0.29	0.24	0.078	0.25	1.24
	60	3.12	0.35	0.22	0.070	0.32	1.60
	65	4.50	0.44	0.32	0.074	0.24	1.39
	70	4.42	0.42	0.30	0.061	0.38	1.41
	80	2.61	0.23	0.52	0.079	0.18	0.44
Bo 4 1972	0	2.86	0.33	0.20	0.041	0.05	1.61
	5	2.63	0.33	0.20	0.052	0.07	1.65
	10	2.65	0.38	0.32	0.046	0.34	1.20
	15	3.08	0.38	0.22	0.060	0.21	1.73
	20	2.98	0.41	0.28	0.069	0.26	1.43
	25	3.54	0.36	0.28	0.067	0.19	1.27
	30	4.00	0.68	0.29	0.072	0.34	2.33
	35	5.27	0.94	0.41	0.090	0.32	2.27
	40	4.10	0.47	0.28	0.091	0.35	1.68
	42.5	4.13	0.69	0.34	0.109	0.44	2.02
	45	3.74	0.46	0.36	0.076	0.21	1.28
	47	3.25	0.32	0.25	0.071	0.15	1.29
	49	3.43	0.51	0.42	0.080	0.41	1.21
	51	2.36	0.34	0.31	0.060	0.23	1.09
	52.5	2.44	0.30	0.27	0.072	0.19	1.14
	53	2.77	0.25	0.18	0.069	0.20	1.39
	55	2.46	0.28	0.27	0.053	0.16	1.06
	57	2.10	0.31	0.35	0.064	0.26	0.90
	59	2.13	0.22	0.20	0.075	0.09	1.12
	62.5	2.78	0.23	0.31	0.059	–	0.73
	65	1.76	0.21	0.21	0.068	0.14	1.00
	67.5	2.40	0.24	0.27	0.100	0.05	0.90
	70	2.75	0.23	0.35	0.065	–	0.65
	72.5	2.66	0.34	0.43	0.054	0.05	0.80
	75	2.88	0.37	0.31	0.069	0.29	1.17
River Vosso 1972		2.41	0.26	0.15	0.061	0.14	1.69

Fig. 5.5

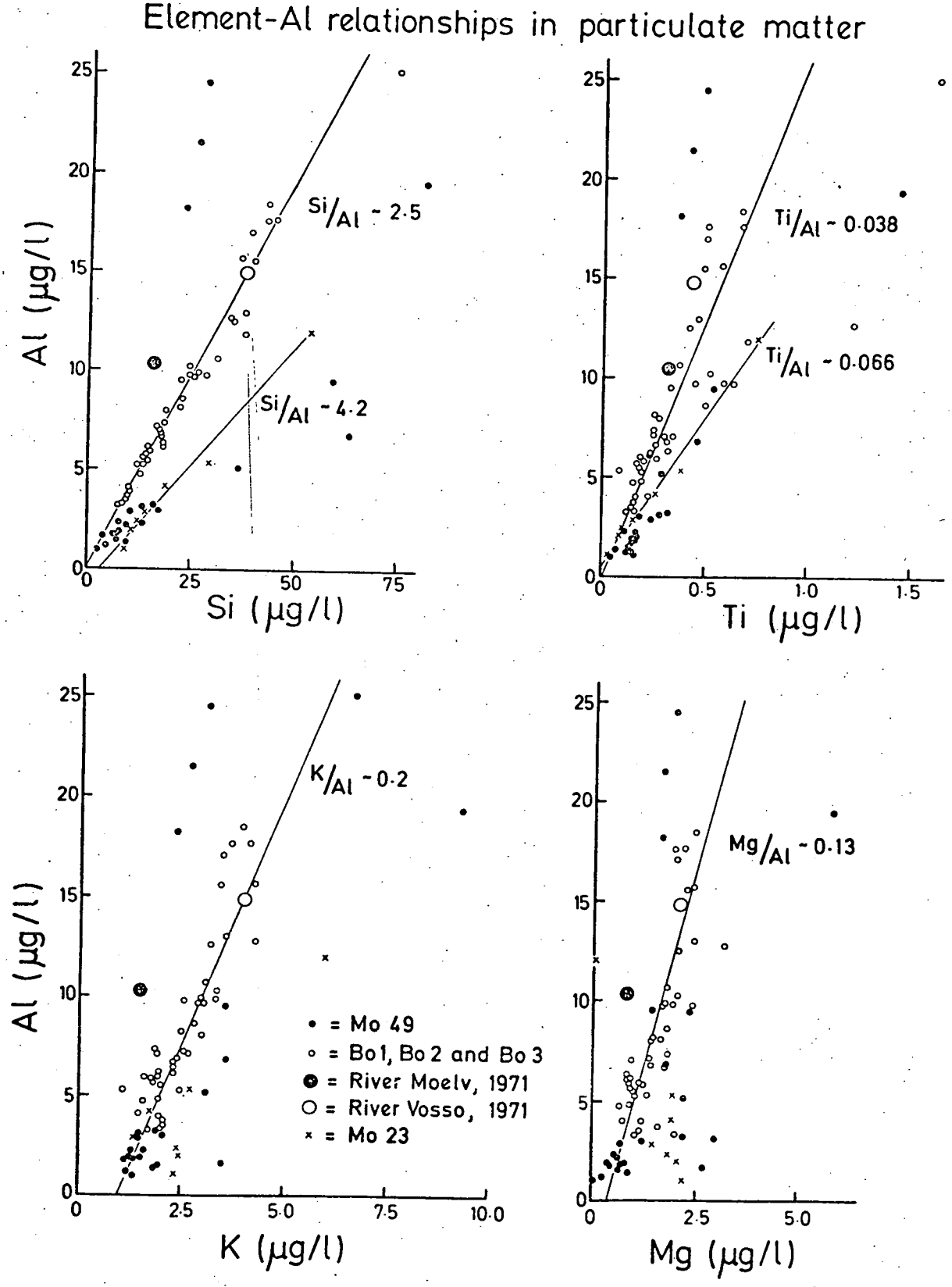
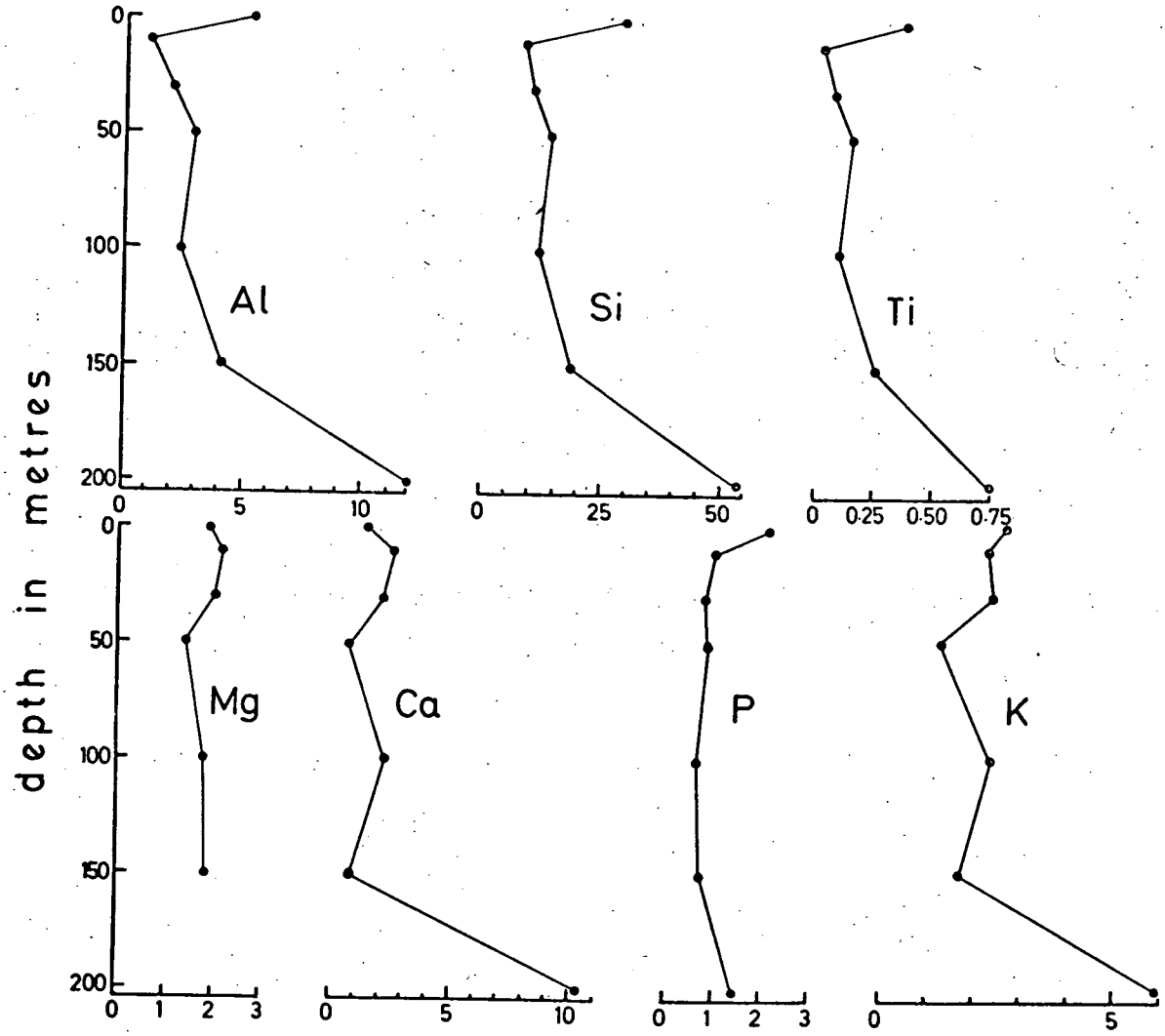

Element-Al relationships in particulate matter
Al (µg/l)
Si (µg/l)
Si/Al ~ 2·5
Si/Al ~ 4·2
Ti (µg/l)
Ti/Al ~ 0·038
Ti/Al ~ 0·066
K (µg/l)
K/Al ~ 0·2
Mg (µg/l)
Mg/Al ~ 0·13
• = Mo 49
◦ = Bo1, Bo 2 and Bo 3
◉ = River Moelv, 1971
○ = River Vosso, 1971
× = Mo 23

Fig. 5.6

Vertical distribution of particulate Al, Si, Ti, K, Mg, Ca and P at Mo 23 (µg/l)



Vertical distribution of particulate Al, Si, Ti, K, Mg, Ca, P and S at Mo 49 and in River Moelv (o). (µg/l)

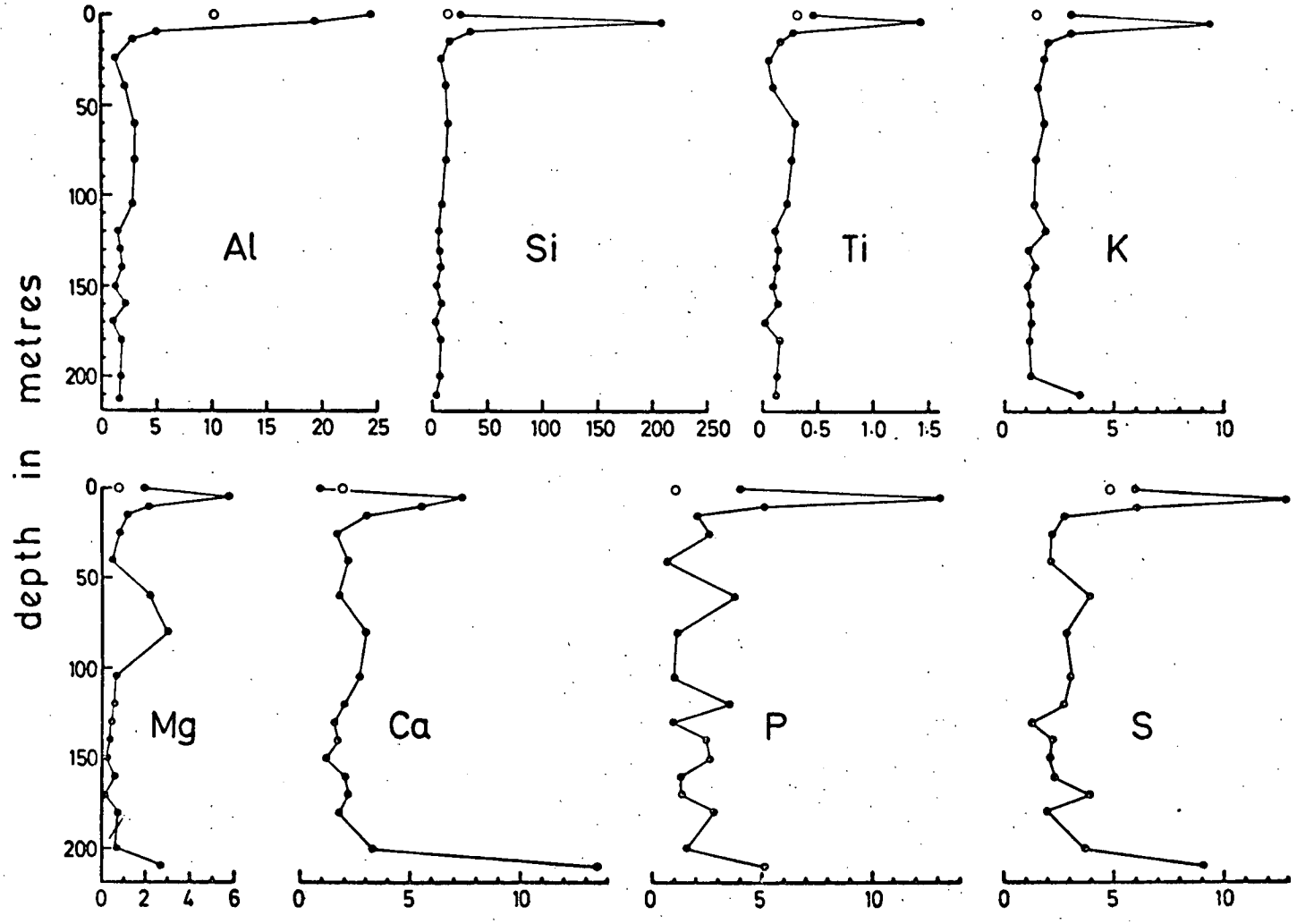


Fig. 5.7

Vertical distribution of particulate Al, Si, Ti, K, Mg, Ca, P and S at Bol and in River Vosso (o). (µg/l).

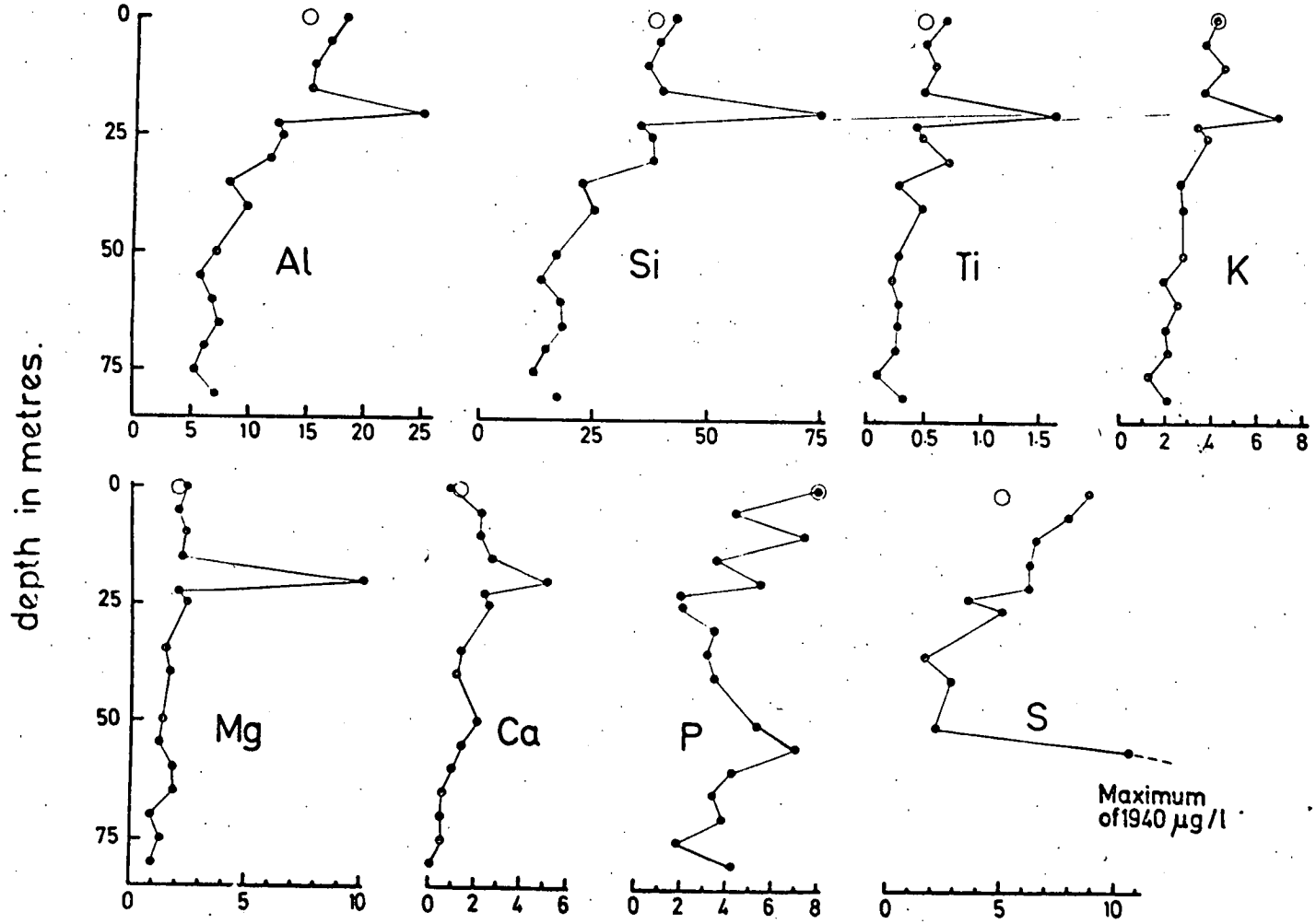


Fig. 5.8

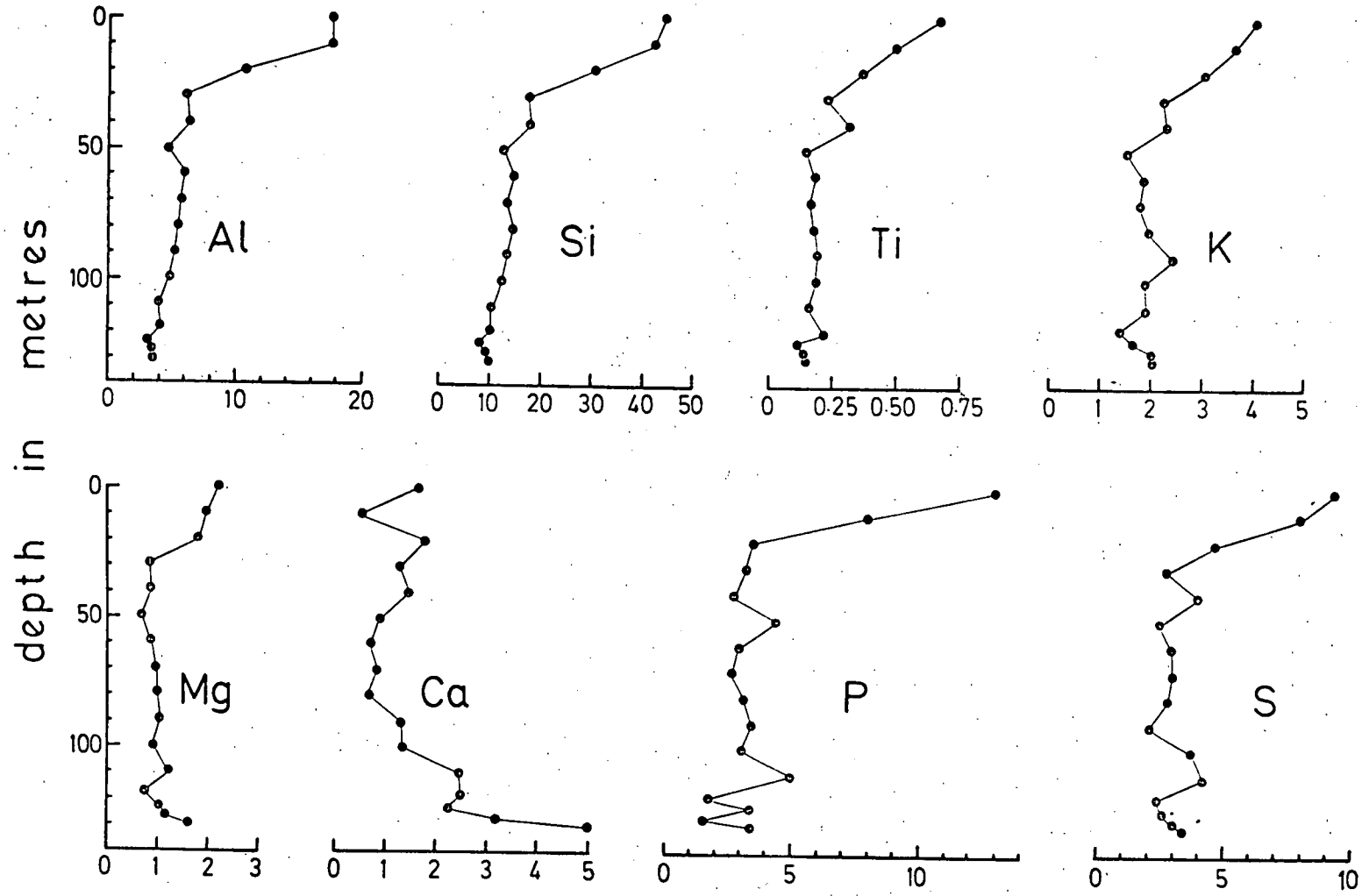

Vertical distribution of particulate Al, Si, Ti, K, Mg, Ca, P and S at Bo 2
(µg/l)
depth in metres
Al
Si
Ti
K
Mg
Ca
P
S
0
50
100
0 10 20
0 10 20 30 40 50
0 0.25 0.50 0.75
0 1 2 3 4 5
0 1 2 3
0 1 2 3 4 5
0 5 10

Fig. 5.9

greater and possibly reflect a slower settling of detritus caused by the marked density stratification (p. 22). Profiles of particulate Al, Ti and Si for stations Mo 23, Mo 49 and Bo 2 are shown in Figs. 5.6, 5.7 and 5.9 respectively. Although in all instances the bottom waters show anomalously high total particulate matter concentrations (see p. 34), only at Mo 23 can this be attributed to detrital silicates as indicated by the distribution of particulate Al, Ti and Si. The deep circulation in Osterfjord at Mo 23 (p. 13) suggests that the bottom maximum here may be due to re-suspension of bottom sediment.

The average Si/Al ratio of the particulate matter in the waters of Bolstadfjord in 1971 was 2.5 (Fig. 5.5 and Table 5.3) compared to ~3.1 in the underlying sediments and to an average value for shales of 3.0 (Krauskopf, 1967). The low value in the particulate matter probably reflects the rapid settling of quartz grains relative to micas and a low standing crop of diatoms at the time of sampling (p. 39). The same ratio averages 4.2 and 4.4 in the particulate matter of Osterfjord and Mofjord respectively, compared to respective values of ~3.4 and ~3.8 in the underlying sediments (see p. 39 for discussion).

The average K/Al and Mg/Al ratios in river and near-surface particulate matter from Bolstadfjord in 1971 were 0.22 and 0.14 respectively, being slightly lower than values representing average shale (Table 5.3). The values of these ratios are higher and more variable below the pycnocline (>29m) while they are intermediate in the underlying sediments. The following year their values had increased in the particulate matter from Bolstadfjord largely because

more particulate K and Mg occurred.

In the particulate matter of Mofjord the K/Al and Mg/Al ratios are far more variable throughout the water column and, except for the surface samples, are invariably higher than in the underlying sediments. In Osterfjord too the ratios are higher in suspended particulate matter than in the sediments but here the particulate matter samples were not corrected for contained salt. Very high K/Al and Mg/Al ratios exist in the particulate matter from the bottom waters at Mo 49 and Bo 2 (Table 5.3; see p. 84 for discussion).

There are several factors that may affect the Mg/Al and K/Al ratios of the particulate matter and produce the high values observed below the pycnocline. Firstly there may have been an error in correcting for the retained sea-salt (Appendix D). However a gross error in this assessment, which is improbable, would be needed to explain some of the ratios. In addition residual salt on the filter papers would result in a relatively low K/Mg ratio instead of a high ratio, as observed in the deep waters (Table 5.3), since there is a lower concentration of K than Mg in sea water. As expected this effect is evident in the sub-surface samples collected at Mo 23 in 1970 which are uncorrected for retained salt (Table 5.3). A second and more likely factor is the rapid settling of non-K and non-Mg bearing aluminium-silicates such as plagioclase feldspars. This mechanism however would also tend to lower the K/Mg ratio as K is likely to be present in both micaceous and orthoclase minerals whereas Mg is probably present mainly as chlorite (p. 49). There is the possibility that fairly rapid adsorption of Mg and K by clay minerals and amorphous

material has occurred. Russell (1970) observed that cation exchange reactions occur when river-borne clay minerals are introduced into the marine environment and that equilibrium is reached within a period of weeks. In absolute terms, Russell observed that Mg was adsorbed to a slightly greater extent than K. This is to be expected in cation exchange reactions occurring in sea water since divalent ions are adsorbed preferentially to monovalent ions (Carroll, 1959) and Mg is more concentrated than K. Russell (op. cit.) remarks however that it is surprising that K was adsorbed to the extent observed because illite comprised only ~5% of the total clay mineral content. It is known that K fixation by leeched micaceous minerals (i.e. illite) occurs to a greater extent than for any other element (Carroll, op. cit.). Since such minerals are likely to predominate in the suspended particulate matter of this study (p. 47) it is probable that K-adsorption occurs to a greater degree than was observed by Russell (op. cit.).

Ti/Al ratios of the particulate matter collected from Bolstadfjord in 1971 (Bo 1, Bo 2 and Bo 3) are lower than those in the following year (Bo 4 and Bo 5) and also lower than the ratios in particulate matter from Osterfjord and Mofjord (Table 5.3). Surface sediment values of Ti/Al for all the fjords range between 0.060-0.069 and are similar to the average value quoted for shale of 0.056 (Krauskopf, 1967). However only in Osterfjord is there a close similarity between the values of the Ti/Al ratio in the particulate matter and sediments (Table 5.3). There are no defined vertical trends in the Ti/Al ratios in the waters examined, with values, especially in

Mofjord, varying erratically with depth. Similar Ti/Al ratios occur in particulate matter from coastal waters off Scotland (Price and Calvert, 1973). These authors suggest that an increase in Ti/Al ratio represents an increase in grain-size of the particulate matter. The completely different range of Ti/Al ratios found in the particulate matter of Bolstadfjord in consecutive years suggests that such a relationship may exist here since this difference is not likely to reflect a change of source material.

5.5 Elements Predominantly Associated with Biogenous Material

The high Si/Al ratios of the particulate matter of Mofjord (Mo 49) and probably Osterfjord (Mo 23) (Fig. 5.5 and Table 5.3) are due for the most part to a large standing crop of diatoms (Fig. 5.2a and b). The values of this ratio are greatest in the near-surface waters of Mofjord and reach a maximum of 10.8 at 5m (equivalent to ~160 µg/l Si in excess of the amount present as silicate minerals if we assume this material to have a Si/Al ratio of 2.5). The generally lower values of the Si/Al ratio in particulate matter from Bolstadfjord (see stations Bo 1-5 in Table 5.3) reflect a smaller standing crop of diatoms (Fig. 5.2c).

Particulate Ca concentrations are shown in Table 5.2. Variations in the Ca/Al ratio of silicate minerals are insufficient to produce the range of values observed in the suspended particulate matter (Table 5.3). The highest Ca/Al ratios, as well as K/Al and Mg/Al ratios, occur in particulate matter from the bottom waters at Mo 49 and Bo 2 and are coincident with exceptional particulate Mn concentrations (see p. 84 for discussion). However most of the

observed variation is almost certainly related to changes in the biogenous contribution of particulate Ca. Although organisms secreting calcium carbonate skeletons, such as coccolithophorids (p. 33), probably account for most of this fraction, diatoms may also be important in this respect. For example the Ca/Si ratio in several species of diatom varies between 0.02 and 0.06 according to Vinogradov (1953) and an even higher ratio has been reported for some Black Sea species (Vinogradova and Koval'skiy, 1962). If these values are correct, it is estimated using a Ca/Si ratio of 0.02 that a significant proportion (a maximum of almost a half) of the particulate Ca exists as diatom frustules.

As with the Si/Al ratio, differences in the Ca/Al ratio of particulate matter imply a much greater standing crop of plankton in Mofjord than in Bolstadfjord. This characteristic is also reflected in the underlying sediments although the absolute values of the Ca/Al ratio are lower (Table 5.3). There was a significant increase in the values of both the Ca/Al and Si/Al ratios in particulate matter from Bolstadfjord in 1972 (Bo 4 and Bo 5) compared to 1971 (Bo 1, Bo 2 and Bo 3) (Table 5.3) suggesting the existence of a larger standing crop of plankton. However changes in the chemical composition of the lithogenous fraction of the particulate matter between the two years as indicated by Ti/Al ratios (p. 39) may also have affected the Ca/Al and Si/Al ratios.

The concentrations of particulate P and S are shown in Table 5.2 and their vertical distributions in Figs. 5.6-5.9. The most striking feature is the exceptionally high concentration of particulate

S present in nearly all samples collected from the anoxic zone of the inner basin of Bolstadfjord (Bo 1 and Bo 3). These concentrations are also high (maximum ~60 µg at./l) relative to the total dissolved sulphide content (maximum ~200 µg at./l). Here the particulate S is thought to be present as elemental S because the concentration of all other major elements is about two orders of magnitude less. This view is supported by a loss of particulate S with time during its analysis under vacuum since elemental S has a relatively high vapour pressure. The question arises of whether the elemental S exists in situ or whether it results from oxidation of dissolved sulphide species during sampling. If present in situ some may be produced by the activity of sulphur bacteria although more probably it would be derived from the oxidation of dissolved sulphide species through mixing between oxic and anoxic waters (see Richards, 1965). Should the latter be the case, the greatest concentrations of elemental S would be expected to occur at or just above the O_2-H_2S boundary especially as the hydrographic data indicates that the deep waters at Bo 1 and Bo 3 are well-stratified and have not been recently disturbed (p. 22) Since particulate S does not exhibit such a trend it is implied that oxidation took place during sampling although the fairly slow kinetics of this reaction (see Richards, 1965; Cline and Richards, 1969) do not altogether support this hypothesis either. In addition some workers (e.g. Cline and Richards, op. cit.) suggest that elemental S is not even a significant product of purely chemical oxidation of reduced S species.

Both particulate P and S may be present to some small extent in the lithogenous fraction. For instance P may exist as apatite, abundant in the probable crystalline source rocks (Kolderup and Kolderup, 1940), or as phosphate ions adsorbed by clay minerals (Carroll, 1959) while S may occur as detrital sulphide minerals, also common in the source rocks, or as adsorbed sulphate ions associated with clay minerals (Carroll, op. cit.). However there is little covariance between particulate P or S and any other element within the oxic waters examined, demonstrating the varying source of these two elements in the waters. Although a significant amount of particulate P and S will be associated with terrestrial organic debris, their most important contribution is probably that from plankton in which both elements are considerably enriched (Bowen, 1966). This is especially true in surface waters where particulate organic matter comprises up to 93% of the total load or 0.62 mg/l (p. 33). Thus the fact that maxima of particulate S and P coincide with that of detrital components at Mo 49 (Fig. 5.7) whereas both elements are concentrated above the pycnocline at Bo 1 (Fig. 5.8) can be explained since they will be associated with the biologically productive zone as well as with detrital constituents. Although variable, the P/S ratio of the particulate matter (except where elemental sulphur exists) averages about unity which is similar to that in plankton and certain terrestrial plants (Bowen, 1966). Particularly high concentrations of particulate P and S exist in the bottom waters at Mo 49 (Fig. 5.7) which are reflected by an equally high content or particulate organic matter (Fig. 5.3). However, high values of particulate P observed

around the O_2-H_2S boundary within the inner basin of Bolstadfjord (see for instance sample from 55m at Bo 1 in Fig. 5.8) are unrelated to changes in the particulate organic matter concentration (see p. 85 for discussion).

It is interesting to note that particulate P and S concentrations in Bolstadfjord support the contention that a greater standing crop of plankton existed there in 1972 than in 1971. The amount of particulate P relative to that of detrital lithogenous material in the waters, as indicated by P/Al ratios, is between one and two orders of magnitude greater than in the underlying sediments. This is a reflection of the biomass occurring within the water column (e.g. the standing crop of plankton) and the regeneration of organically bound P in the deeper waters and underlying sediments (p. 27). The S/Al ratios of the particulate matter (0.3-5.6; exclusive of samples from anoxic waters in Bolstadfjord) are almost invariably greater than those of the underlying sediments although this is obviously more marked in the oxic sediments (0.01-0.04) than in the anoxic sediments (0.04-0.6). In a similar way this demonstrates the regeneration of organically bound S despite the fact that the element's distribution is complicated by sulphide precipitation (pp. 53 and 86).

CHAPTER 6

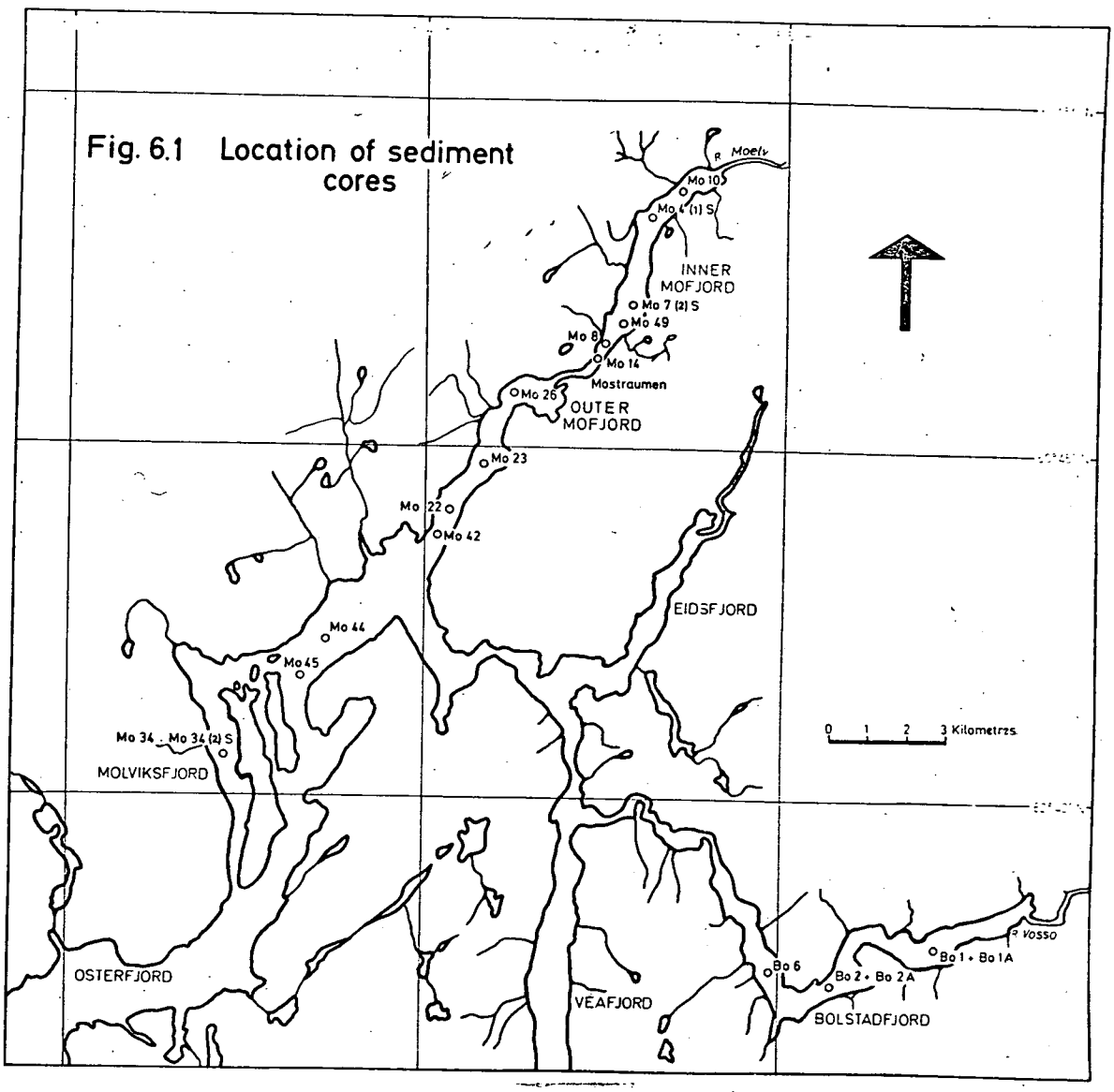
THE SEDIMENTS

6.1 Introduction

Two main sediment facies, 'marginal' and 'basin', are evident as in other fjord basins (Gucluer and Gross, 1964; Doff, 1970). Their distribution is related to the morphology of the basins. Sediments of the 'marginal' facies represent coarse-grained and occasionally thin deposits, often only of shell debris, occurring on shallow rock ledges at the sides of the basins. The 'basin' facies sediments are restricted to the deep, flat floors of the fjords and are generally finer-grained. Little or no sediment cover exists on the steep fjord walls that separate these contrasting environments.

Only 'basin' facies sediment cores were collected during 1970 and 1971 (Fig. 6.1). The cores from Mofjord, Molviksfjord and Osterfjord were sub-sampled at intervals varying between 2cm and 10 cm. Those from Bolstadfjord were sub-sampled according to lithology. The sampling techniques are described in more detail in Appendix A and core logs are given in Appendix E. Dried samples ($110^{o}C$) were analysed in bulk for major elements (Ca, K, Fe, Ti, Si, Al, Mg, P, Mn, S and C) and for trace elements (Rb, Sr, Zr, Y, Nb, Ni, Zn, Cu, Pb and Mo). The Cl content of the sediment samples was also determined in order that a correction could be made to those elements (S, Mg, Ca, K and Sr) present in residual sea salt (Appendix D). With the exception of C, the analysis of all elements was carried out

Fig. 6.1 Location of sediment cores



using X-ray fluorescence spectrometry (Appendix C). Total-C was determined by combusting the sample in a LECO induction furnace and carbonate-C or "CO_2" by acid treatment (HCl) and measurement of the CO_2 evolved (Appendix C). The difference between these two values is taken to be the organic-C content. The mineralogy of some sediment cores was determined by X-ray diffractometry (Appendix C). A complete set of analytical results is given in Appendix D along with a correlation matrix (Kandall Rank) for the sediments as a whole.

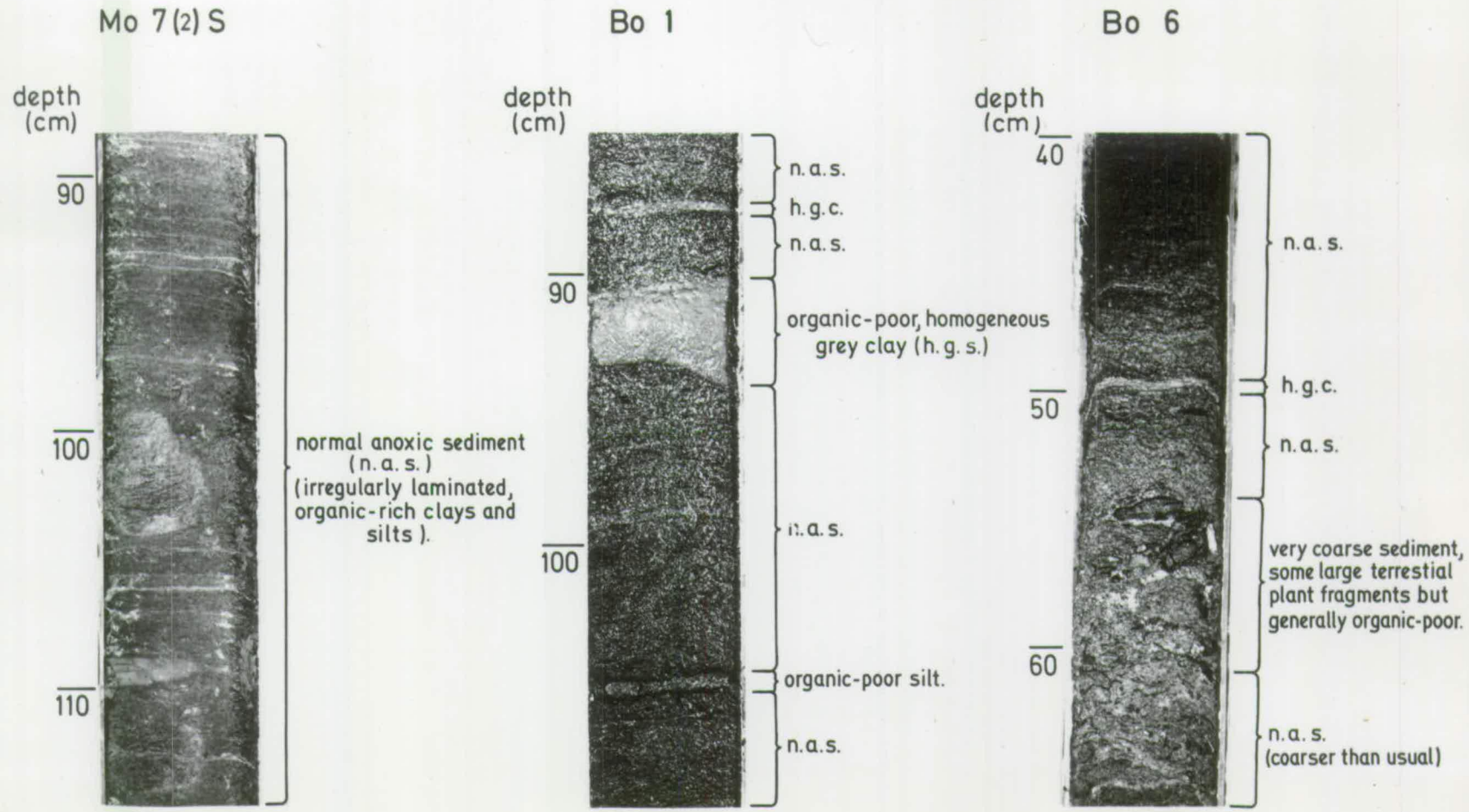
6.2 Description of the Sediments

The sediments in Osterfjord differ considerably from the others being mainly blue-grey or green-grey coloured, homogeneous clays and silts. Certain horizons contain shell material, mostly fragmented and complete bivalves, and terrestrial organic debris, mainly leaves and twigs. The surface few centimetres of some cores have a reddish-brown colouration. The sediments of Osterfjord are well-compacted and restricted penetration of the coring device. They seem to be devoid of H_2S and will therefore be termed oxic although it is possible that slight sub-surface sulphate reduction may occur.

In contrast the surface sediments (0-5cm) of Mofjord, Bolstadfjord and Molviksfjord are invariably black in colour and comprise organic-rich muds strongly smelling of H_2S. Consequently these sediments will be termed anoxic. At depth however their lithology varies both between fjords and between basins within the same fjord. Sub-surface sediments from Inner Mofjord are similar to the surface sediments there but in addition contain terrestrial organic debris and shell

material in greater abundance than is seen in the oxic sediments. Irregular, light coloured laminations occur throughout the length (maximum 130cm) of all cores from this basin and suggest the absence of any burrowing organisms and strong bottom currents (Calvert, 1964). In the following discussion this type of sub-surface lithology will be referred to as 'normal' anoxic sediment (see core Mo 7(2)S in Fig. 6.2). The irregular vertical distribution of laminations compared for instance with the 'varved' sediments of Saanich Inlet (Gross et al., 1963) and Drammensfjord in southern Norway (Strøm, 1936; Doff, 1970) is due to the typically irregular runoff of the rivers of western Norway (Strøm, op. cit.). The sub-surface sediments of Outer Mofjord are similar to those in the inner basin except that they are not laminated and show instead the presence of polychaete dwelling tubes. The core (Mo 26) from the outer basin and the two cores (Mo 8 and Mo 14) from just inside the inner basin contain exceptionally large amounts of shell material. It is thought that much of the sediment in these two areas is derived by slumping from the shallow sill at Mostraumen where deposits comprising predominantly shell debris are accumulating. In Molviksfjord there is a sharp break in the sediments at ~45cm between 'normal' anoxic deposits and an olive-green coloured, homogeneous clay that exists down to at least 105cm. In Bolstadfjord the sub-surface sediments vary greatly both vertically within a core and between the three basins of the fjord. In addition to the 'normal' anoxic sediment, occasional horizons of organic-poor, homogeneous, light grey clay and of coarse rock fragments (maximum of 2cm diameter), shells, leaves and

Fig. 6.2 CORE SECTIONS SHOWING MAJOR TYPES OF LITHOLOGY



twigs occur in some cores (see cores Bo 1 and Bo 6 in Fig. 6.2). Slumping and turbidity currents are thought to be a relatively common feature of fjord sedimentation (e.g. Pickard, 1961; Holtedahl, 1965) and therefore provide a plausible explanation of the observed coarse horizons particularly since the latter cannot be traced from one basin to another and thus suggest that their origin is associated with a form of transport occurring below sill depth. Sub-marine clay slides in fjords have been observed on several occasions (e.g. Terzaghi, 1957; Rosenqvist, 1960) and are the probable cause of the grey clay horizons in the sediments of Bolstadfjord. Strøm (1936) also attributed this mechanism to explain clay horizons in Drammensfjord sediments.

6.3 Mineralogy

The qualitative mineralogy of cores Bo 1 and Bo 6 was determined. Quartz ($I_{3.34\text{Å}} > I_{4.26\text{Å}}$), alkali feldspars (3.24Å - c.f. Jørgensen, 1965), plagioclase feldspars (4.04Å - c.f. Peterson and Goldberg, 1962), and micaceous material or illite ($I_{10\text{Å}} \gg I_{5\text{Å}}$) are the predominant minerals present. The sharp and symmetrical character of the 10Å reflection suggests that the illite is fine-grained and well-crystallised (Weaver, 1961). There is invariably a significant peak at 7Å and often smaller ones at 14Å and 4.7Å; in all cases $I_{7\text{Å}} \gg I_{4.7\text{Å}} > I_{14\text{Å}}$. Chlorite is therefore present as it has a series of basal reflections at 14Å, ~7Å, 4.7Å and 3.5Å of which the 4.7Å peak is diagnostic (Biscaye, 1964). Kaolinite has a series of basal reflections at ~7Å, 3.57Å, 2.35Å and 1.8Å and thus may also occur. A small 2.71Å reflection is always present and is attributed to pyrite. The

main amphibole peak (8.5Å) occurs in some diffraction traces. A halite peak (2.82Å) always occurs and is due to residual sea salt in the sediments. Other minerals that may be present in small amounts but have not been identified are montmorillonite (14Å) and mixed-layer illite-montmorillonite (11.5-11.1Å). No peak that could be attributed to a mixed Ca, Mg, Mn carbonate was observed in any of the traces. The bulk mineralogy is very similar to that described for Fennoscandian glacial and post-glacial clays (e.g. Collini, 1950; 1956; Wiklander, 1950; Rosenqvist, 1955; Graff-Petersen, 1957; Jørgensen, 1965; McNamara, 1966) supporting the view that this material probably represents the source of much of the fjord sediment.

6.4 Major Element Geochemistry

The mean and range of major element concentrations in the fjord sediments are shown in Table 6.1 along with those for comparable types of sediment. The major element concentrations of the different lithologies are shown in Table 6.2 and the element/Al_2O_3 ratios of the sediments in the various fjords are compared in Table 6.3 to those of a gneiss from the Bruvik area (about 20 km to the south of Stamneshella; see Fig. 2.2), Oslofjord sediments and to average shale. Anoxic sediments are sub-divided into four groups (p. 117); 'normal' anoxic sediments; organic-poor sediments comprising the coarse-grained and light grey coloured clay horizons in Bolstadfjord; shelly sediments; and Mn-rich sediments.

a) Elements dominantly associated with the lithogenous fraction of the sediments

Al is predominantly associated with detrital aluminium-silicate

TABLE 6.1

Major element concentrations
in the fjord and comparable sediments (wt.%)

	1	2	3	4	5	6
CaO	4.21 2.02-14.29	3.63 1.92-7.30	0.93	2.49	2.21	5.50
K_2O	2.83 1.75-4.10	3.33 2.27-3.81	3.26	2.00	3.61	1.31
Fe_2O_3 (total)	6.15 3.13-9.42	8.08 6.48-10.43	8.23	5.49	6.89	1.40
MnO (total)	0.18 0.02-1.93	1.31	0.48	0.10	0.11	-
TiO_2	0.73 0.45-1.17	0.67	0.84	0.63	0.77	0.25
SiO_2	52.30 32.72-67.19	49.60 34.85-59.01	55.34	66.53	58.62	78.33
Al_2O_3	13.04 7.12-18.12	13.60 8.77-15.48	17.84	13.51	16.63	4.77
MgO	2.03 0.56-4.46	2.42 1.77-2.97	3.42	2.11	2.60	1.16
P_2O_5	0.30 0.15-0.66	0.34	0.14	0.14	0.16	0.08
CO_2	1.28 0.00-9.24	2.10 0.08-6.45	0.35	-	-	5.03
Org C	4.55 0.38-9.32	3.27	0.31	0.43*	1.10*	0.80
S	1.35 0.07-3.01	1.04	-	0.12	0.24	0.03

1. Average and range of 174 samples - this study
2. Average and range of 13 Oslo Fjord sediments (Doff, 1970)
3. Average argillaceous pelagic sediments (Chester, 1965)
4. Average greywacke (Wedepohl, 1968)
5. Average shale (Wedepohl, 1968)
6. Average sandstone (Clarke, 1924)

* total C

TABLE 6.2

Major element concentrations in the main lithologies (wt.%)

	1	2	3	4	5
CaO	4.54 3.81–6.04	3.34 2.25–6.41	2.54 2.02–3.01	2.57 2.12–3.81	8.95 5.75–14.29
K_2O	3.50 3.34–3.71	2.74 1.75–3.90	3.22 2.37–4.10	2.80 2.27–3.98	2.49 2.03–3.00
Fe_2O_3	6.62 5.49–7.39	5.79 3.55–7.68	6.41 3.36–8.35	7.65 5.57–9.42	4.74 3.13–6.81
MnO	0.15 0.05–0.43	0.08 0.03–0.16	0.16 0.06–0.52	0.53 0.10–1.93	0.04 0.02–0.09
TiO_2	0.80 0.73–0.86	0.73 0.46–0.96	0.82 0.54–0.93	0.81 0.70–1.17	0.56 0.45–0.69
SiO_2	54.51 50.43–58.16	53.31 32.72–64.05	59.52 52.35–67.19	49.77 42.40–59.15	48.57 39.93–57.35
Al_2O_3	14.09 13.31–14.89	12.79 7.12–16.14	15.63 13.49–18.12	14.34 12.85–17.59	10.34 9.12–11.42
MgO	2.35 1.96–2.97	1.96 1.16–2.81	2.50 0.86–3.48	2.47 1.99–4.46	1.27 0.56–1.88
P_2O_5	0.27 0.23–0.33	0.29 0.19–0.43	0.26 0.20–0.33	0.39 0.23–0.66	0.23 0.15–0.28
CO_2	1.56 0.84–2.80	0.54 0.00–3.09	0.12 0.00–0.34	0.30 0.00–1.27	4.74 0.78–9.24
Org C	2.20 1.58–3.16	5.04 1.34–9.32	1.18 0.38–2.29	5.23 0.96–8.00	5.30 1.77–8.64
S	0.17 0.07–0.28	1.54 0.30–2.98	0.59 0.34–0.90	1.80 0.58–2.84	1.43 0.57–3.01

1. Oxic sediments (21 samples)
2. Normal anoxic sediments (76 samples)
3. Organic-poor anoxic sediments (11 samples)
4. Mn-rich anoxic sediments (37 samples)
5. Shelly anoxic sediments (29 samples)

TABLE 6.3

Major elements/Al_2O_3 ratios in sediments from the various basins

	Number of samples	$\frac{SiO_2}{Al_2O_3}$	$\frac{TiO_2}{Al_2O_3}$	$\frac{K_2O}{Al_2O_3}$	$\frac{Fe_2O_3}{Al_2O_3}$	$\frac{CaO}{Al_2O_3}$	$\frac{MgO}{Al_2O_3}$	$\frac{MnO}{Al_2O_3}$	$\frac{P_2O_5}{Al_2O_3}$
Osterfjord sediments	21	3.87 3.70-4.06	0.056 0.053-0.063	0.25 0.23-0.27	0.47 0.40-0.52	0.31 0.28-0.42	0.17 0.14-0.21	0.011 0.004-0.030	0.019 0.016-0.023
Mofjord sediments	68	4.57 4.20-5.20	0.054 0.045-0.080	0.23 0.19-0.26	0.43 0.28-0.71	0.49 0.19-1.57	0.13 0.05-0.34	0.005 0.002-0.012	0.021 0.014-0.031
Molviksfjord sediments (0-50cm)	8	4.49 4.31-4.63	0.058 0.050-0.064	0.24 0.22-0.27	0.55 0.46-0.64	0.90 0.63-1.26	0.16 0.14-0.18	0.006 0.005-0.008	0.026 0.022-0.028
Molviksfjord sediments (50-80cm)	3	3.74 3.69-3.78	0.056 0.055-0.057	0.27 0.26-0.28	0.48 0.47-0.49	0.33 0.32-0.34	0.18 0.18-0.19	0.007 0.007-0.007	0.019 0.018-0.019
Bolstadfjord - inner basin sediments	32	3.84 3.46-4.96	0.058 0.040-0.067	0.19 0.17-0.22	0.46 0.25-0.56	0.18 0.15-0.22	0.16 0.06-0.19	0.007 0.004-0.011	0.023 0.014-0.030
Bolstadfjord - middle and outer basin sediments	42	3.48 2.96-4.56	0.055 0.041-0.079	0.20 0.17-0.24	0.52 0.30-0.66	0.18 0.11-0.26	0.17 0.11-0.30	0.035 0.007-0.135	0.024 0.013-0.043
Oslofjord sediments[1]	12	3.7	0.050	0.24	0.59	0.15	0.18	0.143	0.025
Gneiss from Vaksdal, Bruvik[2]		4.43	0.037	0.15	0.34	0.22	0.12	0.003	0.013
Average shale[3]		3.52	0.046	0.22	0.41	0.13	0.16	0.007	0.010

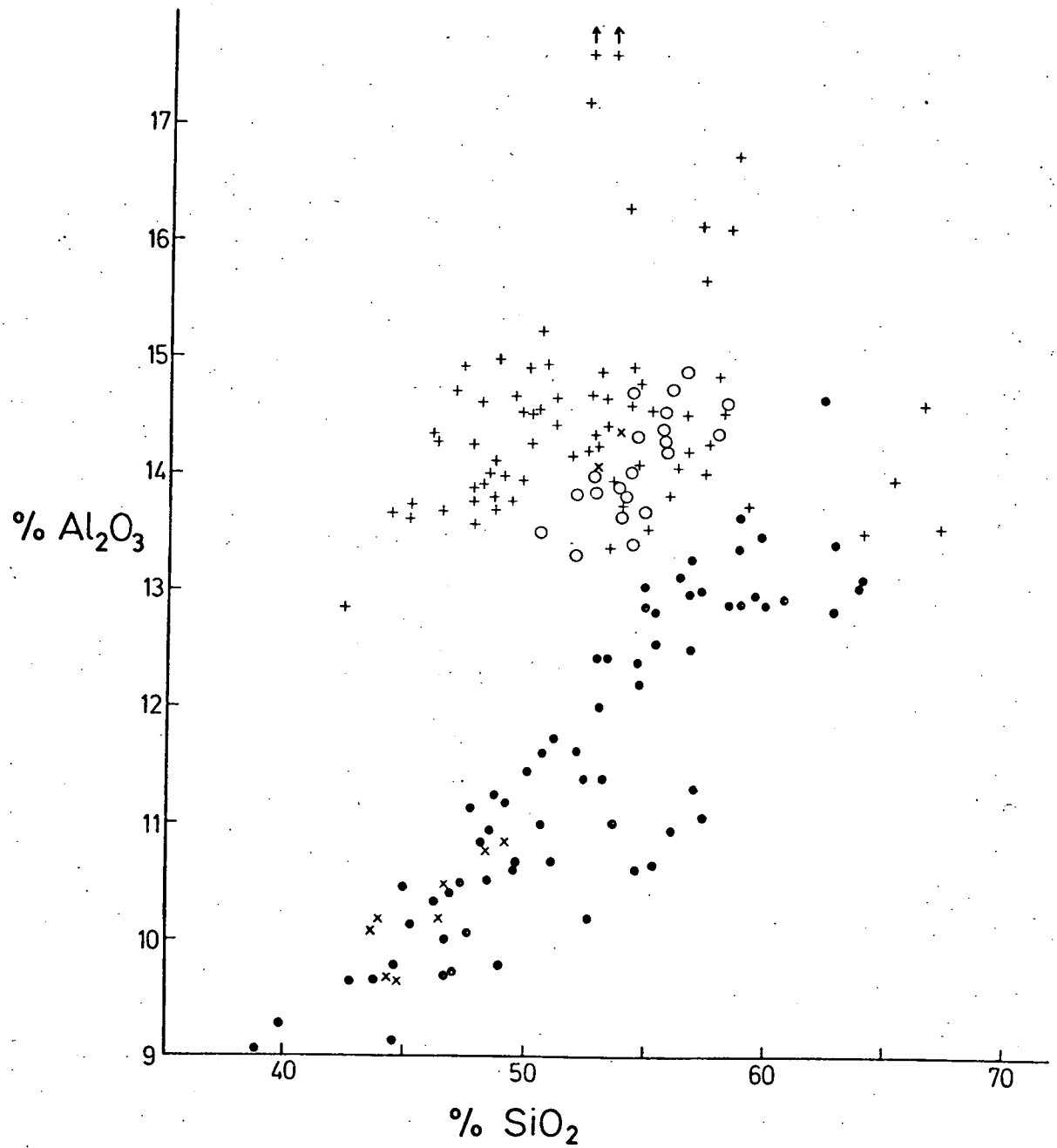
1. Average values according to Doff (1970)
2. After Kolderup and Kolderup (1940)
3. After Wedepohl (1968)

minerals, mainly feldspars and clays, and therefore the element is used as an indicator of this group of minerals (Chester, 1965). Si generally correlates well with Al but different SiO_2/Al_2O_3 ratios exist in the sediments of the various fjords (Fig. 6.3 and Table 6.3), probably reflecting differences in the plankton productivity within the water column and in the relative concentrations of detrital quartz and aluminium-silicate minerals (pp. 36 and 39). An inverse relationship between Si and Al in some Bolstadfjord sediments, especially in the organic-poor horizons, implies some dilution of clay mineral content by quartz. A similar relationship exists in sediments from the Gulf of Paria, Venezuela (Hirst, 1962). Surprisingly some of the grey clay horizons as well as the coarse horizons have exceptionally high SiO_2/Al_2O_3 ratios (maximum 4.9). Fine-grained quartz however, is being brought into Bolstadfjord via runoff at the present time (p. 32) and is known to be a common constituent of fine-grained sediments associated with a glacial origin (see Biscaye, 1964).

The relationship between Mg and Al is less complex although Mg is generally more closely related to Fe, Mn and Ti probably due to their mutual association with Fe-Mg minerals (e.g. chlorite). Clay minerals are in fact the only abundant Mg-bearing mineral type present and Mg is therefore a reasonable indicator of their concentration. In this respect the MgO/Al_2O_3 ratio varies as much within one fjord as it does between fjords and varies little with depth within most cores. The coarse horizons in the sediments of Bolstadfjord are notable exceptions having particularly low ratios (Table 6.4), therefore

Fig. 6.3

SiO_2 - Al_2O_3 relationship in the sediments



o = Osterfjord sediments
• = Mofjord sediments
× = Molviksfjord sediments
+ = Bolstadfjord sediments

TABLE 6.4

Element/Al_2O_3 ratios in cores Bo 1 and Bo 6

Depth (cm)	$\frac{SiO_2}{Al_2O_3}$	$\frac{TiO_2}{Al_2O_3}$	$\frac{K_2O}{Al_2O_3}$	$\frac{Fe_2O_3}{Al_2O_3}$	$\frac{CaO}{Al_2O_3}$	$\frac{MgO}{Al_2O_3}$	$\frac{MnO}{Al_2O_3}$	L
Bo 1								
0-1.5	3.56	0.061	0.18	0.56	0.16	0.18	0.007	N
1.5-3.5	3.46	0.060	0.19	0.50	0.16	0.17	0.007	N
3.5-5.5	3.46	0.059	0.18	0.47	0.17	0.18	0.006	N
5.5-9	4.00	0.061	0.19	0.41	0.18	0.14	0.006	C
9-15	3.47	0.058	0.18	0.52	0.17	0.18	0.009	N
15-20	3.68	0.048	0.19	0.47	0.18	0.16	0.007	N
20-22	4.74	0.067	0.18	0.41	0.22	0.16	0.006	G
22-30	3.71	0.060	0.18	0.47	0.18	0.18	0.006	N
30-40.5	3.90	0.060	0.18	0.47	0.18	0.17	0.006	N
40.5-45	3.62	0.054	0.20	0.43	0.17	0.18	0.006	G
45-53.5	3.51	0.056	0.22	0.42	0.15	0.17	0.005	G
53.5-60	4.06	0.063	0.19	0.54	0.20	0.19	0.008	N
60-71	3.69	0.059	0.18	0.48	0.18	0.16	0.007	N
71-81	3.90	0.059	0.19	0.45	0.19	0.15	0.009	N
81-90	3.99	0.060	0.18	0.47	0.19	0.18	0.011	N
90-93	4.68	0.062	0.17	0.39	0.22	0.16	0.006	G
93-100	3.70	0.061	0.18	0.54	0.18	0.18	0.010	N
100-105	4.05	0.057	0.18	0.39	0.19	0.14	0.006	N
105-106	4.96	0.040	0.19	0.25	0.17	0.06	0.004	C
106-120	4.09	0.063	0.18	0.46	0.19	0.15	0.007	N
Bo 6								
0-2	3.39	0.056	0.17	0.55	0.19	0.18	0.098	N
2-4	3.52	0.057	0.18	0.54	0.18	0.18	0.046	N
4-6	3.45	0.058	0.18	0.59	0.17	0.17	0.040	N
6-8	3.52	0.057	0.19	0.50	0.19	0.17	0.059	N
8-10	4.00	0.058	0.19	0.39	0.20	0.14	0.012	N
10-17	3.46	0.062	0.19	0.55	0.19	0.18	0.038	N
17-23	3.32	0.057	0.20	0.50	0.17	0.18	0.032	N
23-35	3.24	0.055	0.20	0.59	0.20	0.20	0.112	N
35-38	3.04	0.050	0.22	0.48	0.13	0.18	0.022	G
38-51	3.21	0.054	0.20	0.63	0.20	0.19	0.135	N
51-57	3.99	0.052	0.21	0.42	0.20	0.15	0.017	N
57-65	3.93	0.052	0.21	0.45	0.18	0.16	0.017	N
65-71	3.58	0.055	0.20	0.58	0.19	0.17	0.049	N
71-74	3.65	0.047	0.21	0.47	0.17	0.16	0.020	C
74-80	3.79	0.053	0.21	0.49	0.18	0.15	0.018	N
80-86	4.56	0.041	0.24	0.30	0.16	0.11	0.008	C
86-98	3.37	0.049	0.20	0.58	0.18	0.19	0.070	N
98-103	3.57	0.057	0.20	0.60	0.18	0.15	0.022	N

L = Lithology

N = Normal anoxic sediment
C = Coarse anoxic sediment
G = Grey clay

suggesting a low clay content. There is no enrichment of Mg in the shelly horizons, in fact they have lower than average MgO/Al_2O_3 ratios.

The only marked deviations from the mean TiO_2/Al_2O_3 ratio (0.059) occur in Bolstadfjord sediments where the values vary between 0.040 and 0.079 and are invariably low in the coarse-grained sediment horizons (Table 6.4). The latter implies either an association of Ti with clay minerals or a relative preponderance of Al over Ti in the coarse horizons. In the former instance this relationship has been attributed to the deposition of very finely divided, amorphous or crystalline TiO_2 along with clay minerals (Goldschmidt, 1954; Degens, 1965). The principal K-bearing minerals are alkali feldspars and illite, and therefore it is not surprising that the K_2O/Al_2O_3 ratio varies little with depth in any of the cores relative to the MgO/Al_2O_3, TiO_2/Al_2O_3 and SiO_2/Al_2O_3 ratios (Table 6.4). The similar geochemical character of the sediments from different fjords, as indicated by MgO/Al_2O_3, TiO_2/Al_2O_3 and K_2O/Al_2O_3 ratios (Table 6.3), suggests that the sediment source material also has a uniform composition although it is apparently not akin to the gneissic rock from the area around Bruvik.

b) Calcium and CO_2

The major Ca-bearing silicate minerals are the plagioclase feldspars although clay minerals and amphiboles will also contribute significant amounts of the element. Despite this, in most of the sediments there is a negative correlation between Ca and Al, and a strong positive correlation between Ca and CO_2 (Fig. 6.4) which

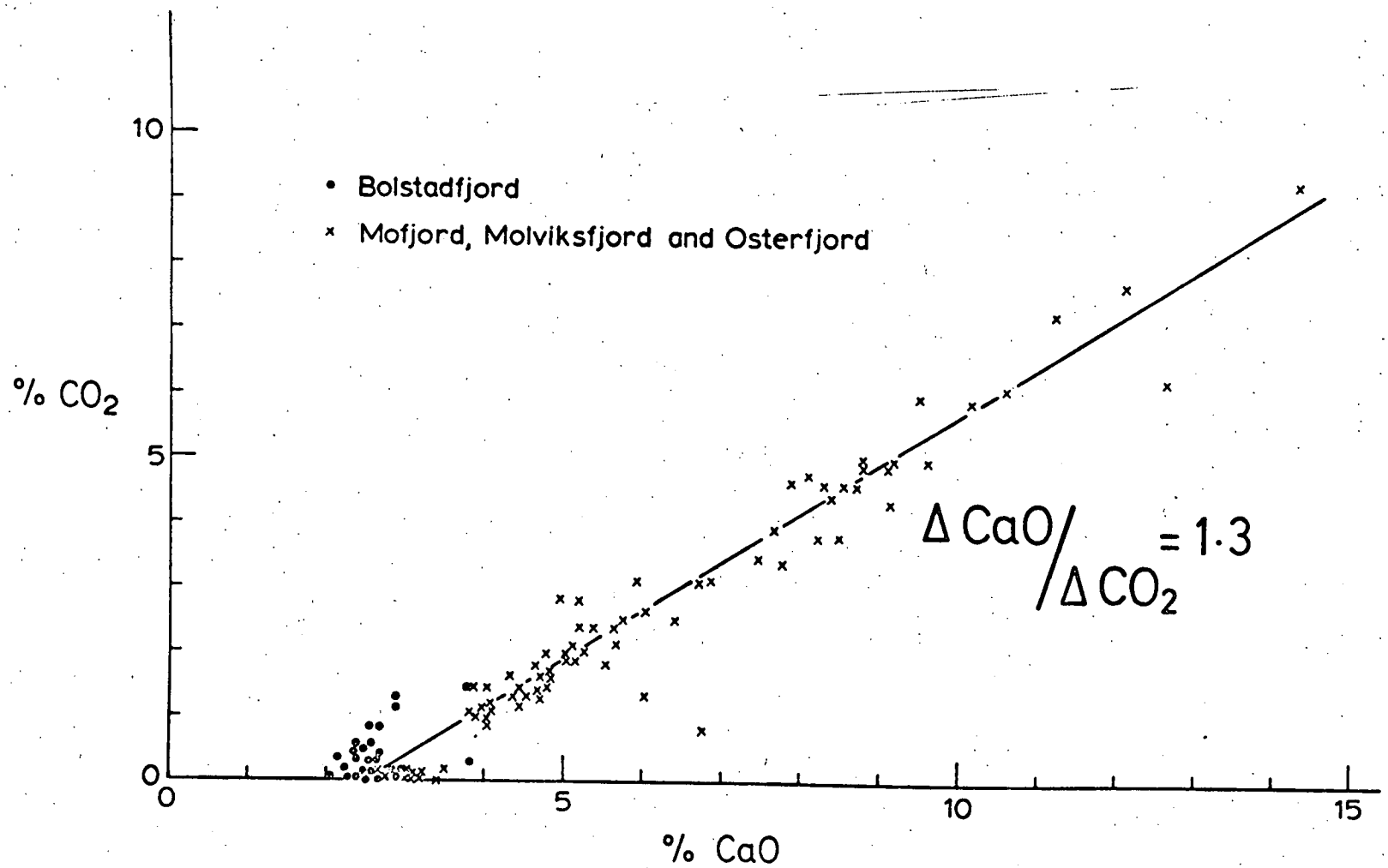
reflect the abundance of shell material and its diluting effect on the lithogenous fraction. The variation in CaO/Al_2O_3 ratios of sediments from the various fjords (Table 6.3) illustrates the location of the most shelly sediments. As there is no observable shell material (bivalves) in Bolstadfjord sediments, the CaO/Al_2O_3 ratio (0.18) is probably roughly that contained in the lithogenous fraction and is similar to the value (0.15) of Oslofjord sediments (Doff, 1970). The CaO/CO_2 ratio of the shell material is ~1.3 (Fig. 6.4) compared with a weight percent ratio of 1.27 for pure $CaCO_3$. Anomalous CO_2 concentrations exist in some horizons of cores Bo 2, Bo 2A and Bo 6 (Fig. 6.4) and are discussed on page 53 .

c) Iron and manganese

Fe, Mn and Mg are closely interrelated in the sediments reflecting their association with ferromagnesian silicates such as chlorite. The correlation of Fe and Mn with Al is less well defined. A proportion of the Fe and Mn is likely to occur as non-silicates in most sediments and both elements are probably affected by diagenesis during sediment burial. In the case of Fe such changes are largely obscured by lithological variation because of the high content of the element in the lithogenous fraction of the sediment. Hence small variations in Fe_2O_3/Al_2O_3 ratios (Tables 6.3 and 6.4) are as much a function of lithology as of diagenesis. In contrast diagenesis of Mn, as denoted by vertical changes in MnO/Al_2O_3 ratios, is well marked. The sediments that do not contain any apparent non-silicate Mn have a MnO/Al_2O_3 ratio varying between 0.002 and 0.012 which is similar to the range in most Oslofjord sediments examined by Doff (1970).

Fig. 6.4

$CaO - CO_2$ relationship in sediments



Two sediment cores (Mo 44 and Mo 45) of the five collected in Osterfjord are considerably enriched in Mn and correspond to those having reddish-brown surfaces. This coloured layer was disturbed during sampling in both instances which explains why the Mn enrichment is not restricted to the surface sediments (0-2cm) (see Appendix D). There is no significant difference between the Fe_2O_3/Al_2O_3 ratios of these sediments (Mo 44 and Mo 45) and any others analysed, even from anoxic environments. It is thought likely however that the reddish-brown surface layer is due to the presence of small quantities of Fe(III) hydrated oxides in addition to those of Mn(IV) as is known in sediments from similar environments (e.g. Gorham and Swaine, 1965; Doff, 1970). Cores Mo 44 and Mo 45 are located in a deep basin of Osterfjord (~440m) while cores Mo 22, Mo 23 and Mo 42 are from a shallower shelf area to the north (~220m) and show no Mn enrichment or reddish-brown surface colouration. A similar relationship between bathymetry and oxide surface layers has been observed in Oslofjord (Doff, 1970) and Loch Fyne, Scotland (Calvert and Price, 1970). Doff (op. cit.) suggests that this may be due to a lack of water movement and a slower rate of deposition in the deeper parts of basins. Evidence from the particulate matter study shows considerable resuspension of bottom sediment in the shelf area of Osterfjord (see station Mo 23; p. 36) inferring the presence of significant bottom currents there. Unfortunately no evidence in this context exists for the deep basin.

Anoxic sediments from the outer and middle basins of Bolstadfjord (Bo 2, Bo 2A and Bo 6) have high and variable Mn contents and

MnO/Al_2O_3 ratios (Tables 6.2. and 6.3). Here Mn appears to be related to CO_2, particularly in core Bo 6 (Fig. 6.5), suggesting the existence of a Mn carbonate. It is reasonable to assume that nearly all of this CO_2 is chemically related to Mn since the sediments in Bolstadfjord (Bo 1 and Bo 1A) not containing any non-silicate Mn have a very low CO_2 content (maximum of 0.30%). In core Bo 6 (Fig. 6.5) Δ MnO/Δ CO_2 corresponds to a theoretical composition of $(Mn_{0.87} X_{0.23})CO_3$. Mn carbonates are known to occur in a variety of environments including other fjord sediments. The variation in their chemical composition is demonstrated in Table 6.5; it is noticeable that the carbonate in core Bo 6 is relatively Mn-rich and that Ca, for the most part, corresponds to X in the above formula. Positive relationships for Mn and CO_2 contents and those of Ca do exist in this core although CaO/Al_2O_3 ratios do not show similar trends (Table 6.6). This may be due to a variation of the Ca held relative to Al in aluminium-silicates since the lithology of the sediments in Bolstadfjord is so heterogeneous (p. 46).

d) Sulphur, phosphorus, and organic C

The anoxic sediments exhibit higher (0.34-3.01% S) and more variable S concentrations compared with the oxic sediments of Osterfjord (0.07-0.28% S). In the latter, S is probably associated mainly with the detrital fraction although its concentration does increase slightly with depth and suggests that an additional source of S may exist. Certainly the high S concentrations in the anoxic sediments are due to the fixation of the element in a variety of forms other than detrital material. For example pyrite is seen in the X-ray

Fig. 6.5

$MnO - CO_2$ relationship in cores Bo 2 and 2A (o), and Bo6 (x)

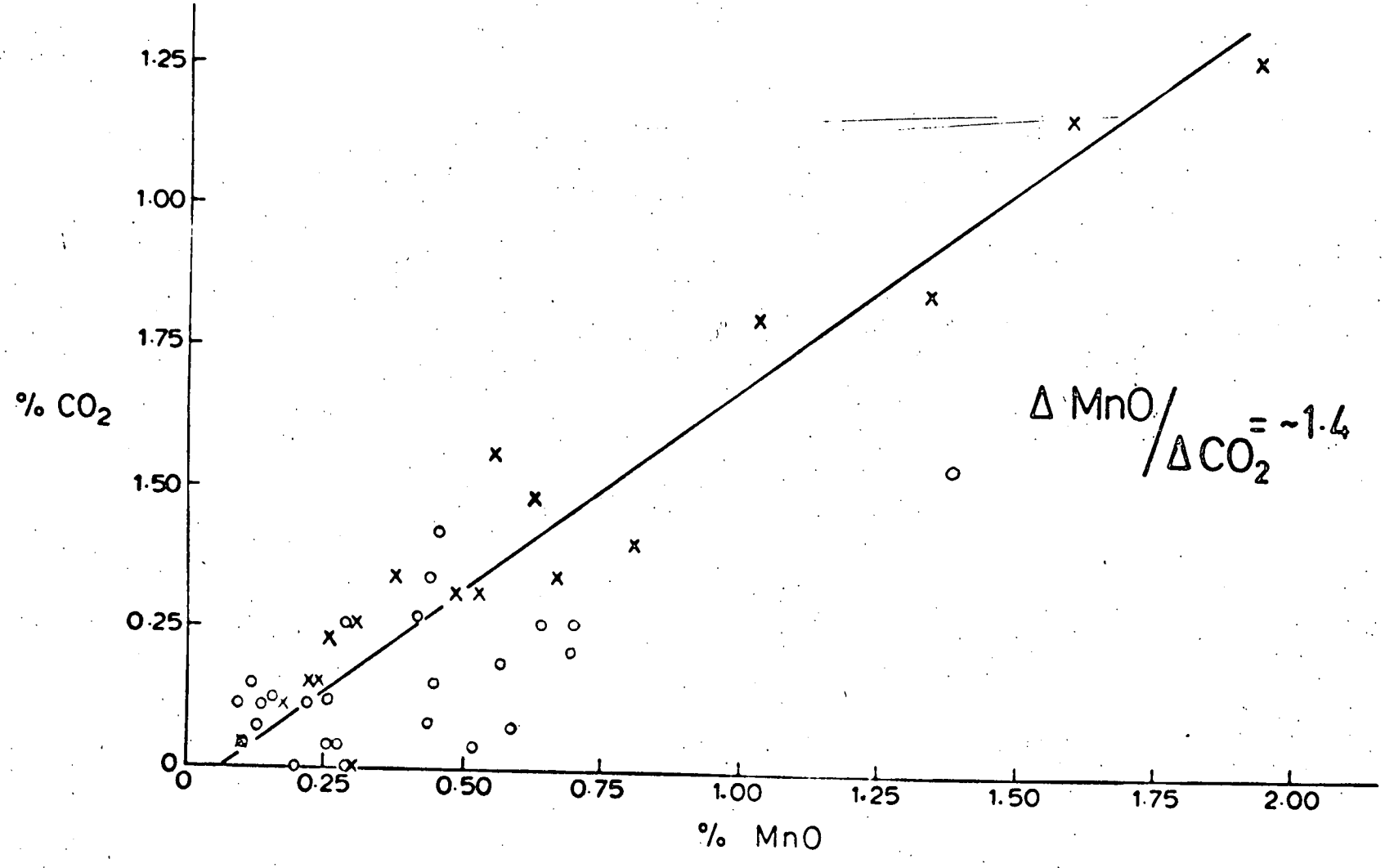


TABLE 6.5

Chemical composition of Mn-rich carbonates in Recent sediments

Location and reference	Composition
Peru Trench (Zen, 1959)	$MnCO_3$
Baltic Sea (Manheim, 1961)	$(Mn_{70}\ Ca_{30})CO_3$ to $(Mn_{60}\ Ca_{32}\ Mg_8)CO_3$
Baltic Sea (Hartmann, 1964)	$(Mn_{56.4}\ Ca_{25.5}\ Mg_{9.7}\ Fe_{8.0})CO_3$
Lake Pinnus-Yarvi, Karelia (Shterenberg et al., 1966)	$(Mn_{50.6}\ Ca_{45.3}\ Fe_{4.0})CO_3$ to $(Mn_{34.2}\ Ca_{28.9}\ Fe_{37.1})CO_3$
Loch Fyne, Scotland (Calvert and Price, 1970)	$(Mn_{47.7}\ Ca_{45.1}\ Mg_{7.2})CO_3$
Bunnefjord, Norway (Doff, 1970)	$\sim(Mn_{50}\ Ca_{50})CO_3$
Bolstadfjord, Norway (this study)	$\sim(Mn_{87}\ X_{23})CO_3$

TABLE 6.6

Vertical distributions of MnO, CO_2, CaO and CaO/Al_2O_3 in core Bo 6

Depth (m)	Lithology	MnO % wt.	CO_2 % wt.	CaO % wt.	$\frac{CaO}{Al_2O_3}$
0-2	N	1.34	0.85	2.56	0.19
2-4	N	0.63	0.48	2.48	0.18
4-6	N	0.56	0.56	2.40	0.17
6-8	N	0.81	0.40	2.69	0.19
8-10	N	0.18	0.11	2.92	0.20
10-17	N	0.53	0.31	2.64	0.19
17-23	N	0.49	0.31	2.59	0.17
23-35	N	1.59	1.16	2.88	0.20
35-38	G	0.38	0.34	2.16	0.13
38-51	N	1.93	1.27	2.87	0.20
51-57	N	0.23	0.15	2.61	0.20
57-65	N	0.24	0.15	2.47	0.18
65-71	N	0.67	0.34	2.58	0.19
71-74	C	0.30	0.00	2.54	0.17
74-80	N	0.26	0.23	2.55	0.18
80-86	C	0.11	0.04	2.40	0.16
86-98	N	1.03	0.80	2.66	0.18
98-103	N	0.31	0.26	2.52	0.18

N normal, anoxic sediment

G organic-poor, homogeneous grey clay

C organic-poor, coarse sediment

diffractograms of anoxic sediments (p. 47) and is likely to have formed *in situ*. These sediments are intensely black in colour suggesting that non-stoichiometric iron sulphides (hydrotroilite) are also present (p. 86). While total Fe in the anoxic sediments appears to be correlated with S this does not necessarily reflect their association in Fe(II) sulphides but more likely illustrates that sediments having a high clay content, and hence a high Fe content relative to one of Al, contain the greatest amount of authigenic sulphide. Kaplan et al. (1963) show that in addition to pyrite and hydrotroilite, S can occur as elemental S, organic S and free sulphide in sediments.

Two major sources of organic matter are likely to contribute towards the organic C content of the sediments; they are runoff (terrestrial origin) and *in situ* productivity (marine origin). Organic C concentrations in the sediments range from 0.38% to 9.32%. It is difficult to obtain a true estimate of the total organic matter content because of differences in composition between the two types present. Organic C invariably comprises a large proportion of the sediments in Mofjord and in the surface 50cm in Molviksfjord, a highly variable proportion in Bolstadfjord sediments, and a low proportion in Osterfjord sediments. In other words the oxic sediments generally have a lower organic C content than the anoxic sediments (Table 6.2). There is also a very high correlation between organic C and S in the sediments as a whole (see Appendix D). The reason for this relationship is not as obvious as it may at first appear. Richards (1965) noted that as a consequence of lowered

redox potentials, greater amounts of organic matter tend to be laid down under anoxic rather than under oxic conditions implying there is a chemical explanation for the observed relationship between S and organic C. However, it is known from a study of the Santa Barbara Basin (Sholkovitz, 1973) that sediments in which considerable sulphate reduction occurs can have a low organic C content (2-2.5%) which is similar to that in sediments where there is little or no sulphate reduction. In addition oxic Oslofjord sediments have organic C concentrations of up to nearly 5% while those that are anoxic have as little as 1% organic C (Doff, 1970; the use of 'oxic' and 'anoxic' here is similar to that in the present study). The evidence suggests that any covariance between organic C and S in sediments reflects a lithological association rather than a chemical one (see also Fe and S); certainly this appears to be true for the sediments from the Bergen area. For example the lowest S (0.34%) and organic C (0.38%) concentrations in the anoxic sediments occur in the coarse and light grey clay horizons of Bolstadfjord. This is probably due to the rapid deposition of these horizons (p. 47) and hence to the dilution of organic matter by inorganic detritus.

Except in those sediments from Bolstadfjord (e.g. core Bo 2) P concentrations are relatively constant (0.15-0.35% P_2O_5) and show no obvious correlation with any other element. There is no significant difference in P content between the oxic and anoxic sediments (Table 6.2). Hence P is probably partitioned between the lithogenous and organic matter fractions of the sediments.

The sediments of Bolstadfjord have exceptionally high P

concentrations (maximum of 0.66% P_2O_5) and an organic C-P relationship exists within them (Fig. 6.6). The observed Δorganic C/ Δ P value is ~76 and the intercept on the P axis is similar to the average P content in sediments from the other fjords. As the organic matter mainly comprises planktonic material (average C/P ratio of ~40) and terrestrial plant material (average C/P ratio ~200; see Bowen, 1966), it is reasonable that the Δorganic C/ ΔP value in the sediments should lie somewhere between these two ratios although this relationship is complicated by diagenetic processes (p. 28). Since there is no evidence to suggest the presence of an authigenic P phase (no covariance between P and Ca or Fe, the two cations most likely to be associated with P), it is probable that the high P concentrations are due to exceptional amounts of organically-bound P. Why organically-bound P should be preferentially retained in Bolstadfjord sediments is not known. It may be associated with differences in sedimentation rates which are probably much greater in Bolstadfjord than elsewhere (p. 46). Alternatively variation in the diagenetic behaviour of organic matter in sediments from different environments may account for this feature.

6.5 Trace Element Geochemistry

The mean and range of trace element contents in all sediments analysed and in sediments of different lithology are shown in Tables 6.7 and 6.8 respectively. In all instances the values lie within the range of concentrations previously reported for comparable sediments.

Fig. 6.6

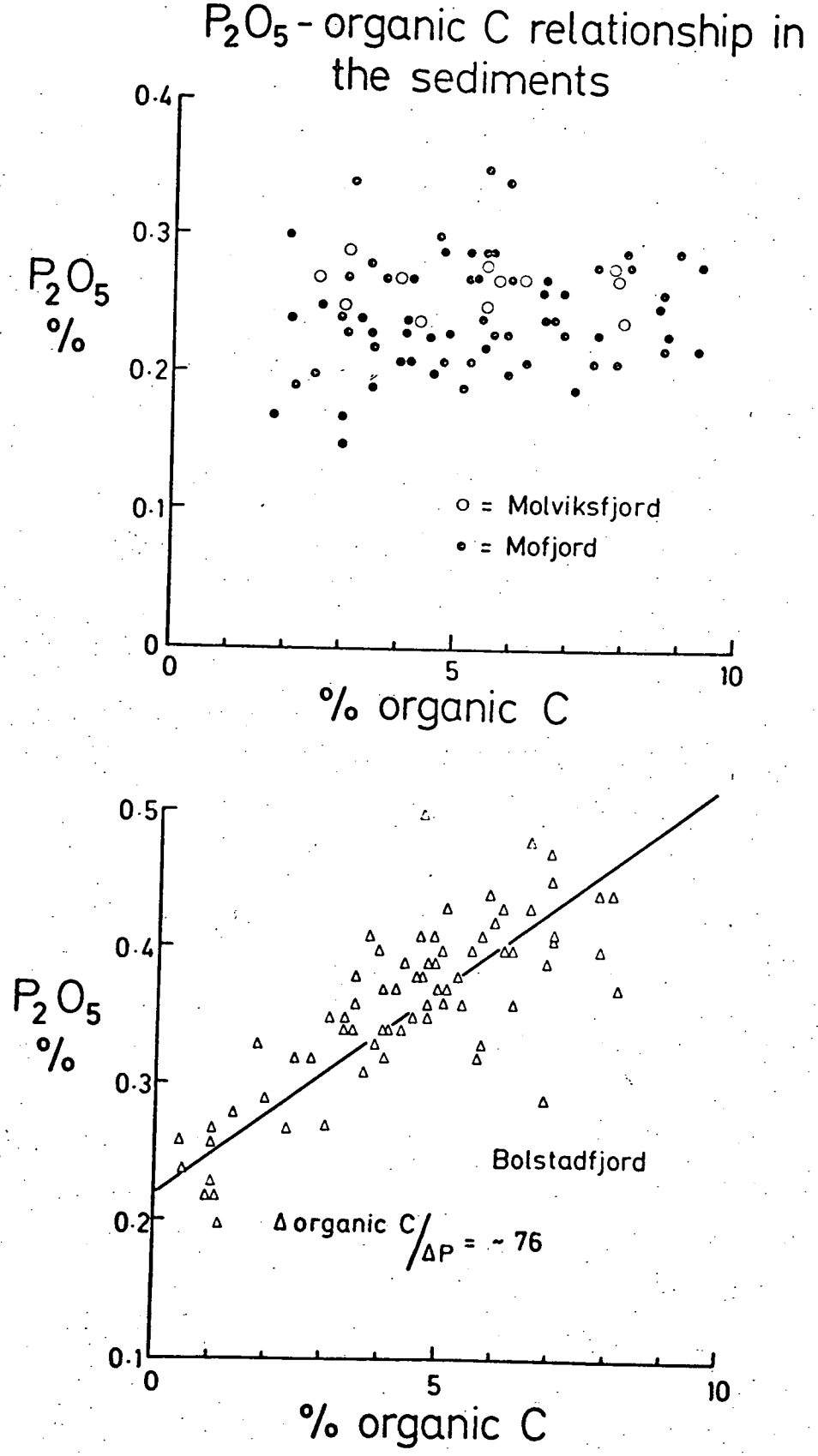

P_2O_5 - organic C relationship in the sediments
P_2O_5 %
0·4
0·3
0·2
0·1
0
0
5
10
% organic C
○ = Molviksfjord
• = Mofjord
P_2O_5 %
0·5
0·4
0·3
0·2
0·1
0
5
10
% organic C
Bolstadfjord
Δ organic C / ΔP = ~ 76

TABLE 6.7

Trace element concentrations
in the fjord and comparable sediments (ppm)

	1	2	3	4	5	6
Sr	356 217-629	223	200	300	-	25-400 2000 ?
Zn	101 41-174	346	60	95	82 48-180	100-1000 10000
Cu	23 6-36	66	45	45	45 30-120	20-300 1000
Pb	35 13-129	104	-	20	-	20-400 ? 700
Mo	32 0-119	7	-	3	26 4-67	10-300 1000
Ni	31 15-48	55	40	68	26 19-34	20-300 2400
Rb	110 78-170	159	80	140	-	450 ?
Nb	14 6-21	28	-	18	-	1 ?
Zr	204 116-368	203	450	160	77 49-120	10-20 ?
Y	43 27-56	38	30	41	21 14-31	-

1. 174 samples - this study (average and range)
2. Median of 114 surface sediments, Oslo Fjord (Doff, 1970)
3. Average greywacke (Wedepohl, 1968)
4. Average shale (Wedepohl, 1968)
5. Average and range of 10 sediments from Saanich Inlet (Gross, 1967)
6. Range and maximum concentrations for black shales (Krauskopf, 1955)

TABLE 6.8

Trace element concentrations in the main lithologies (ppm)

	1	2	3	4	5
Sr	362 336-431	333 253-422	294 217-421	382 248-442	467 325-629
Zn	129 105-169	96 41-174	88 41-119	108 71-172	90 49-159
Cu	24 13-33	23 7-36	20 6-33	26 9-36	22 12-32
Pb	41 20-72	35 13-129	24 16-33	38 19-81	26 14-88
Mo	9 0-13	37 3-72	8 1-20	30 6-54	48 18-119
Ni	34 26-41	28 16-41	37 15-47	36 27-48	26 16-34
Rb	142 122-155	105 85-168	125 87-169	108 94-170	94 78-117
Nb	16 9-21	15 9-21	14 11-19	13 9-18	13 6-18
Zr	183 161-207	217 116-368	224 164-269	203 163-292	179 136-264
Y	44 38-53	44 33-56	44 27-56	45 39-53	39 29-48

1. Oxic sediments (21 samples)
2. Normal anoxic sediments (76 samples)
3. Organic-poor anoxic sediments (11 samples)
4. Mn-rich anoxic sediments (37 samples)
5. Shelly anoxic sediments (29 samples)

a) Trace elements dominantly associated with the lithogenous fraction of the sediments

Rb shows a strong correlation with K (Fig. 6.7) reflecting a close geochemical association (Goldschmidt, 1954). The range of K/Rb ratios is 166-274 (mean = 216) which falls within or slightly above the limits suggested by Heier and Adams (1964) for shales. The relatively high values may be due to the abundance of K-feldspars, which have a higher K/Rb ratio relative to co-existing micas (Heier and Adams, op. cit.; Lange et al., 1966), and to a lack of weathering of the detrital material (Heier and Billings, 1970) as indicated by the well-crystallised nature of the illite. There is as much variation in K/Rb ratios within one basin and even within a core with depth as there is between fjords, supporting the suggestion that the source material of the sediments is geochemically uniform.

Zr is usually held in sediments largely as detrital zircon (Degenhardt, 1957) and the presence of this mineral is indicated within the sediments of the area as Zr correlates more highly with Si than any other element. Furthermore zircon occurs as a common accessory mineral of the area draining into the fjords (Kolderup and Kolderup, 1940). Zr also appears to correlate significantly with Ti, Al and Y in the sediments which may be due to the fact that Zr^{4+} is known to substitute for Ti^{4+} in minerals (Taylor, 1965) and for Al^{3+} in clays (Degenhardt, 1957). The Zr/Al_2O_3 ratio has been used as an indicator of the heavy mineral content of a sediment (Wright, 1972) and the Zr/Rb ratio as a possible marginal facies indicator (Nicholls, 1958). In general the sediments from areas

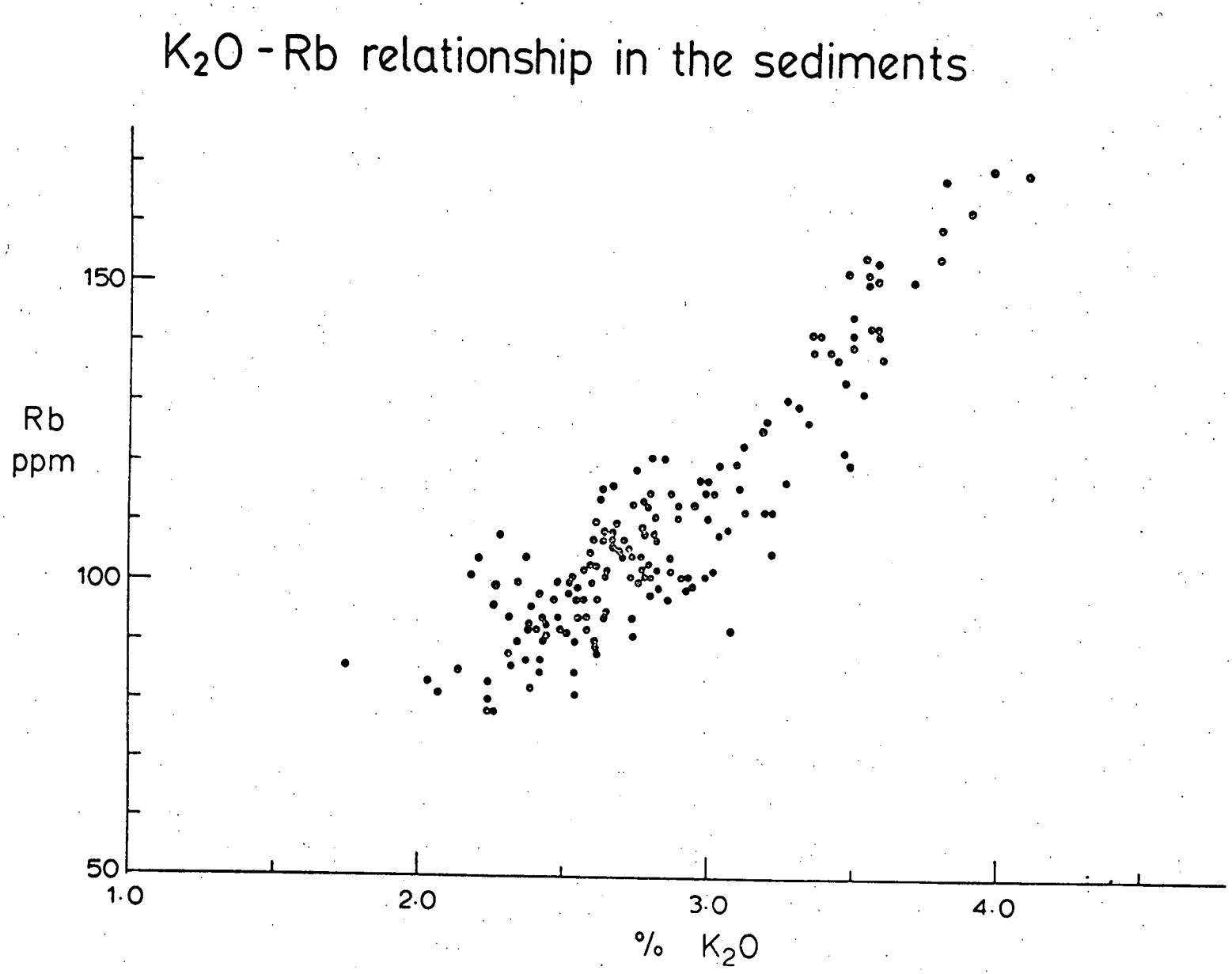

K_2O - Rb relationship in the sediments
Rb
ppm
150
100
50
1·0
2·0
3·0
4·0
% K_2O

Fig. 6.7

close to sources of runoff do have the highest Zr/Rb and Zr/Al_2O_3 ratios. For instance the sediments in core Mo 10, situated near the mouth of the River Moelv, have the highest ratios while the Osterfjord sediments (cores Mo 22, Mo 23, Mo 42, Mo 44 and Mo 45) have the lowest (Table 6.9). In core Mo 10 the two ratios tend to increase at depth, and in core Mo 34(2)S they decrease abruptly below ~45cm implying that significant long-term changes in lithology and hence in conditions of sedimentation may have occurred (p. 67). In all other cores however the ratios show no overall trends with depth suggesting that there has been little long-term variation in conditions of sedimentation at these locations. On the other hand the short-term fluctuations in sedimentation in Bolstadfjord, as denoted by rapid and obvious changes in lithology (p. 46), may be seen in changes in Zr/Rb and Zr/Al_2O_3 ratios (Table 6.9) although these do not always conform to the pattern that coarse-grained sediments necessarily have high Zr/Rb and Zr/Al_2O_3 ratios (Doff, 1970).

Y and Nb appear to be associated mainly with silicate minerals but their distributions neither indicate clearly which silicates nor help in any interpretation of the data. Despite the fact that Ni is greatly enriched in 'black shales' (Table 6.7), there is no significant difference between the Ni contents in the oxic and anoxic sediments (Table 6.8). In fact Ni concentrations in the sediments as a whole are below those of the average shale (Table 6.7). Ni correlates well with Fe, Mg, Mn and Cu, and less so with K, Ti, Al, P, Zn,Rb and Y indicating that the element is associated primarily with ferromagnesian minerals (Taylor, 1965).

TABLE 6.9

Zr/Rb and Zr/Al_2O_3 ratios in sediments from the various basins

Core	Depth (m)	Zr/Rb	$\frac{Zr}{Al_2O_3} \times 10^4$	Core	Depth (m)	Lithology	Zr/Rb	$\frac{Zr}{Al_2O_3} \times 10^4$
Mo 10	0-5	2.5	18	Mo 45	0-2		1.4	14
	5-10	3.1	24		2-4		1.0	12
	10-15	3.0	22		4-6		1.1	12
	15-20	3.3	25		6-8		1.1	12
	20-25	3.7	28		8-10		1.1	12
	25-30	3.4	25					
	30-35	3.7	28					
	35-41.5	3.7	26	Bo 1	0-1.5	N	1.9	14
					1.5-3.5	N	1.9	14
					3.5-5.5	N	2.0	14
Mo 7(2)S	0-10	1.8	15		5.5-9	C	2.2	16
	10-20	2.1	18		9-15	N	2.1	14
	20-30	2.3	19		15-20	N	2.2	16
	30-40	1.7	17		20-22	G	3.1	20
	40-50	1.8	18		22-30	N	2.2	15
	50-60	2.0	17		30-40.5	N	2.2	16
	60-70	2.1	20		40.5-45	G	1.8	14
	70-80	1.8	17		45-53.5	G	1.7	14
	80-90	1.9	16		53.5-60	N	2.3	16
	90-100	1.6	14		60-71	N	2.2	15
	100-110	1.7	15		71-81	N	2.3	16
	110-130	1.7	15		81-90	N	2.6	17
					90-93	G	3.0	19
					93-100	N	2.1	15
Mo 34(2)S	0-10	1.8	16		100-105	N	2.5	15
	10-20	1.8	16		105-106	C	1.8	12
	20-30	1.9	15		106-120	N	2.4	17
	30-40	1.6	15					
	40-50	1.5	16					
	50-60	0.7	8					
	60-70	0.8	9					
	70-80	0.9	10					
Mo 23	0-5	1.6	15	Bo 6	0-2	N	1.9	14
	5-10	1.6	14		2-4	N	2.0	15
					4-6	N	1.9	14
					6-8	N	2.0	15
Mo 22	0-2	1.2	12		8-10	N	2.2	16
	2-4	1.4	15		10-17	N	1.9	14
	4-6	1.3	13		17-23	N	1.8	13
	6-8	1.3	14		23-35	N	1.6	13
	8-10	1.2	12		35-38	G	1.4	12
	10-12	1.3	13		38-51	N	1.7	13
	12-14	1.2	14		51-57	N	1.8	13
					57-65	N	1.7	12
					65-71	N	1.6	12
Mo 42	0-2	1.4	14		71-74	C	1.5	12
	2-4	1.5	15		74-80	N	1.8	13
	4-6	1.5	13		80-86	C	1.5	12
	6-8	1.3	13		86-98	N	1.6	13
					98-103	N	1.8	13
Mo 44	0-5	1.4	13					
	5-10	1.2	12					
				Average shale*			1.1	10
				Average greywacke*			5.6	33

N normal, anoxic sediment

G organic-poor, homogeneous grey clay

C organic-poor, coarse sediment

* data from Wedepohl (1968)

b) Trace elements that are significantly associated with non-lithogenous constituents of the sediments

The average Sr content of the sediments is high relative to that in sediments of comparable lithology (Table 6.7) and the highest Sr concentrations coincide with the most shelly sediments (Table 6.8). The element correlates positively only with Ca and CO_2 while a negative correlation exists between it and most lithogenous elements. This reflects the concentration of Sr in shells and their diluting effect on other constituents of the sediments. The $\Delta Ca/\Delta Sr$ value of the shell material equals ~176 (Fig. 6.8) which falls within the range of values reported for biogenic aragonite (Goldschmidt, 1954). The negligible covariance between Ca and Sr in non-shelly sediments (Fig. 6.8) is not surprising as Sr^{2+} substitutes for K^{+} more readily than for Ca^{2+} in feldspars (Taylor, 1965). Sr may also be held in clay minerals (Chester, 1965). Where carbonate is absent, as in Bolstadfjord sediments, Sr/Rb and Sr/Al_2O_3 ratios show some variations that reflect changes in lithology. For example the coarse and light grey clay horizons often have abnormal but unpredictable ratios as with the Zr/Rb and Zr/Al_2O_3 ratios.

While Cu and Zn correlate with elements indicating that a large proportion of them exists in ferromagnesian minerals particularly in sub-surface sediments (>10cm), a substantial amount of the two elements also appears to occur as non-lithogenous phases. The same is true for Pb although it is associated more probably with feldspars and micaceous minerals (illite) in the lithogenous fraction (Taylor, 1965). Cu, Zn and Pb are also all likely to be adsorbed by clay minerals

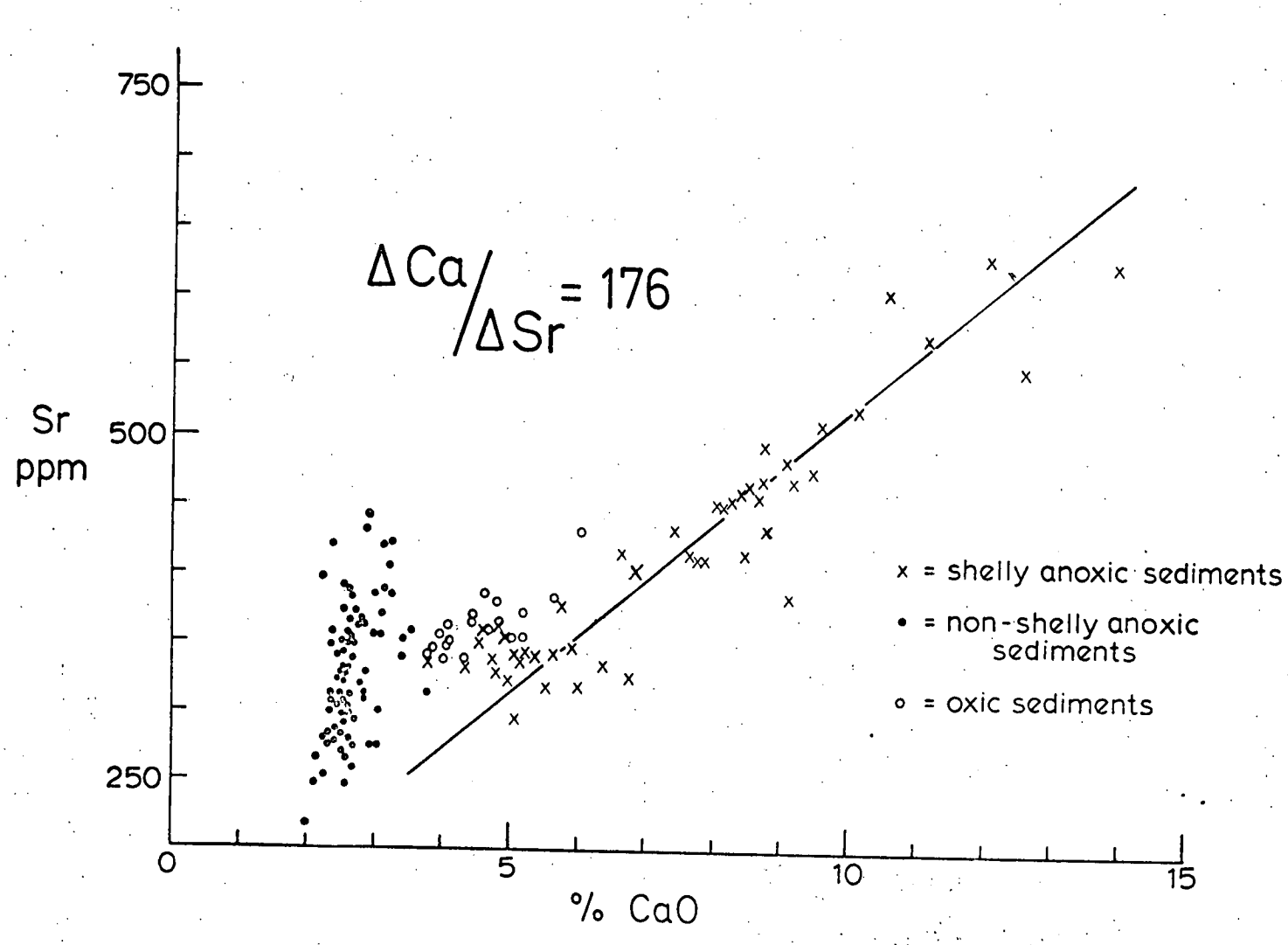

CaO-Sr relationship in the sediments
ΔCa/ΔSr = 176
Sr ppm
750
500
250
0
5
10
15
% CaO
x = shelly anoxic sediments
• = non-shelly anoxic sediments
o = oxic sediments

Fig. 6.8

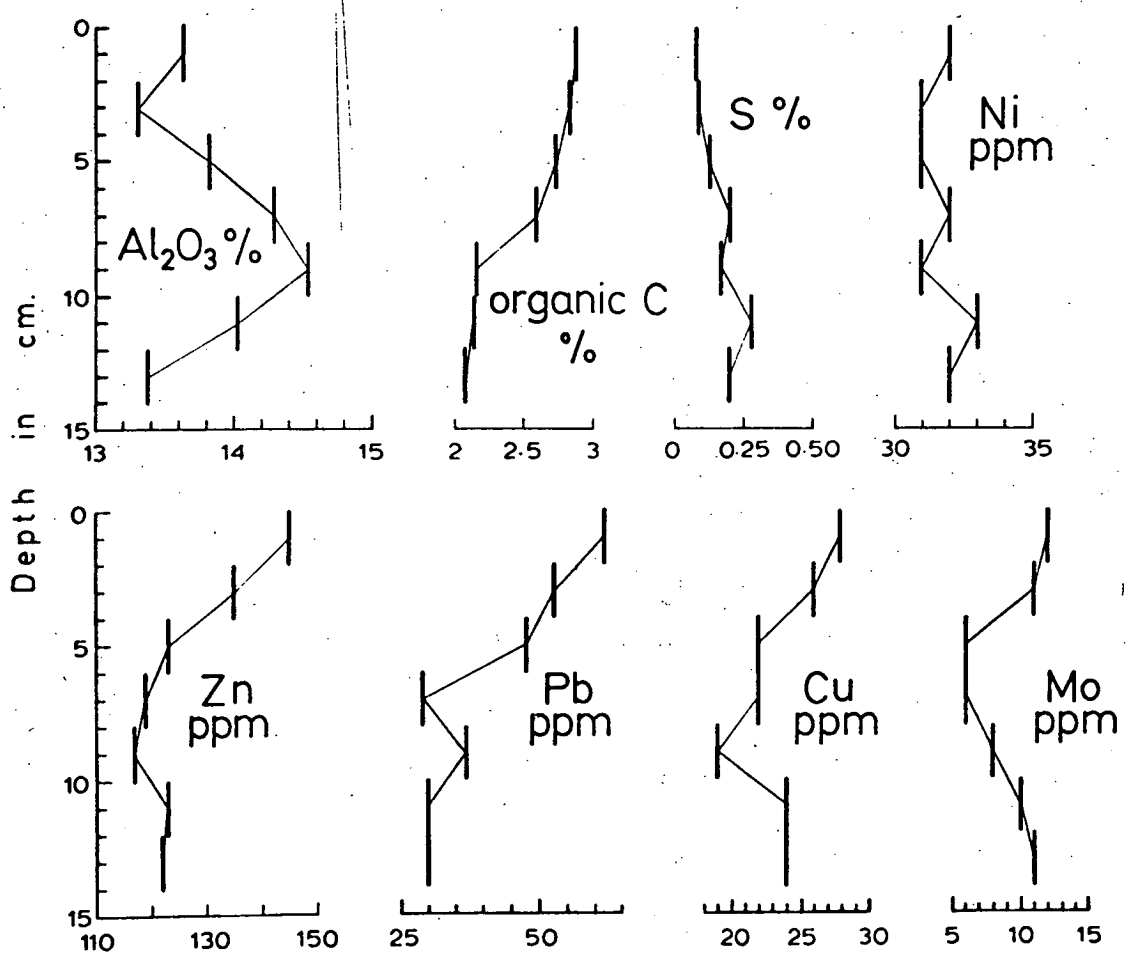
(Chester, 1965). The nature of the non-lithogenous fractions of these elements will be discussed in some detail.

Surface maxima of Zn and Pb occur in every core except Mo 10, a coarse-grained sediment containing much terrestrial plant debris and located close to the mouth of the River Moelv (Fig. 6.1). The maximum surface concentrations of Zn and Pb are 174ppm and 129ppm respectively, which is equivalent to an enrichment factor of about threefold over sub-surface values. Similar surface enrichments of Cu and to some extent Ni and Mo are present in some cores, but these are much smaller both in relation to sub-surface concentrations and in absolute terms, and are often not the highest concentrations within any one core. All the surface maxima usually correspond to high metal/Al_2O_3 ratios and sometimes also to high metal/organic C and metal/S ratios compared to sub-surface sediments (Figs. 6.9-12 and Table 6.10). High metal/S and metal/organic C ratios occur in sub-surface sediments as well, but here they are usually the result of low S and organic C concentrations rather than of high metal concentrations. Within the surface sediments there is no obvious correlation between the metals and organic C, S or even Al. Furthermore no significant differences in the concentrations of Zn, Cu and Pb or in their ratios against Al_2O_3 occur between the oxic and anoxic sediments (Tables 6.8 and 6.10). Metal contents relative to those of S and organic C are significantly higher in Osterfjord sediments (oxic) as they have relatively low S and organic C concentrations.

The distributions of Pb, Zn and Cu in sub-surface sediments

Fig. 6.9

Comparison of vertical distributions of Ni, Zn, Pb, Cu and Mo with those of Al_2O_3, organic C and S in core Mo 22



Comparison of the vertical distributions of Zn, Pb, Cu, Ni and Mo with those of Al_2O_3, organic C and S in core Mo 7(2)S

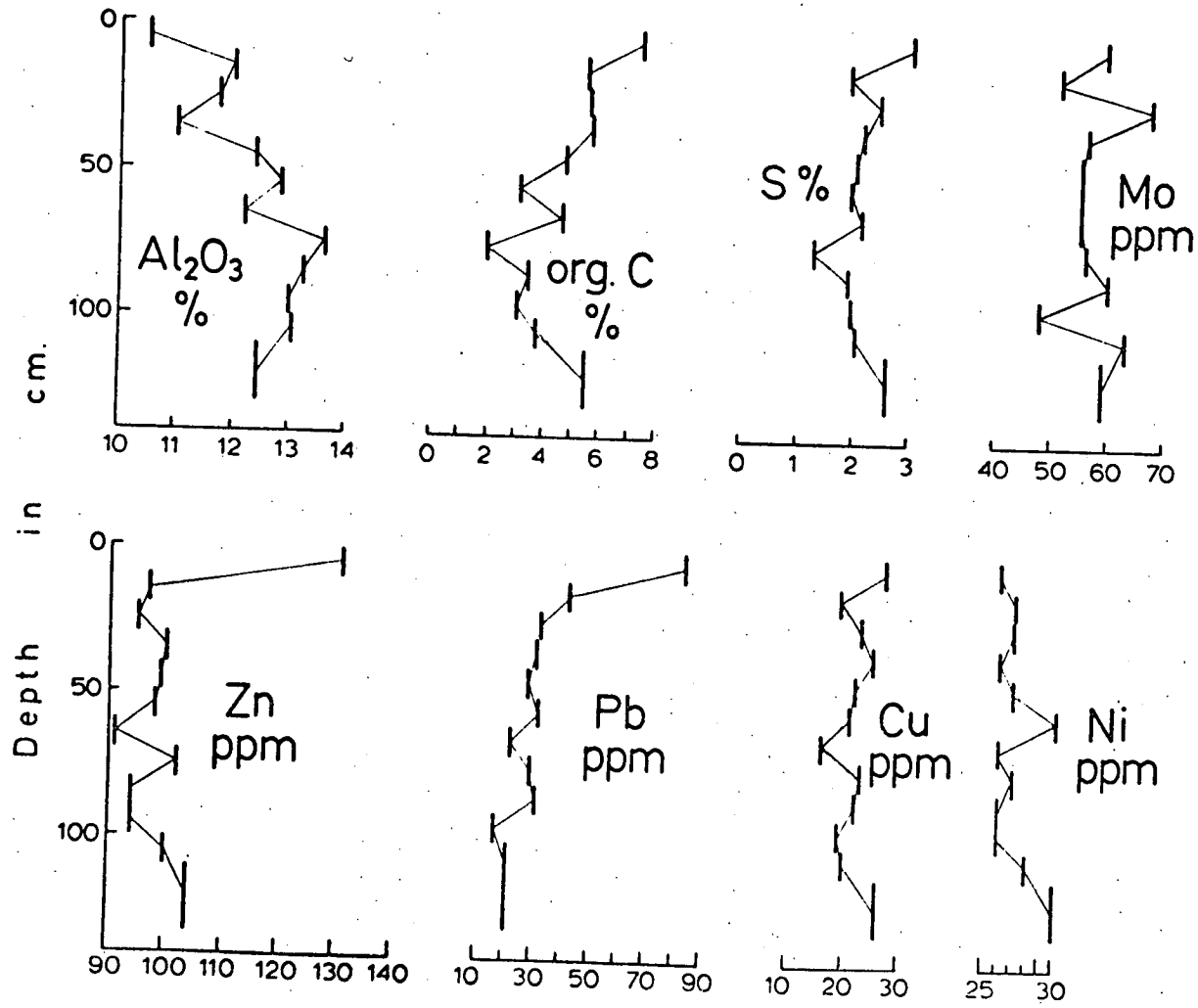


Fig. 6.10

Fig. 6.11

Comparison of the vertical distributions of Zn, Pb, Cu, Mo and Ni with those of Al_2O_3, organic C and S in core Bo1

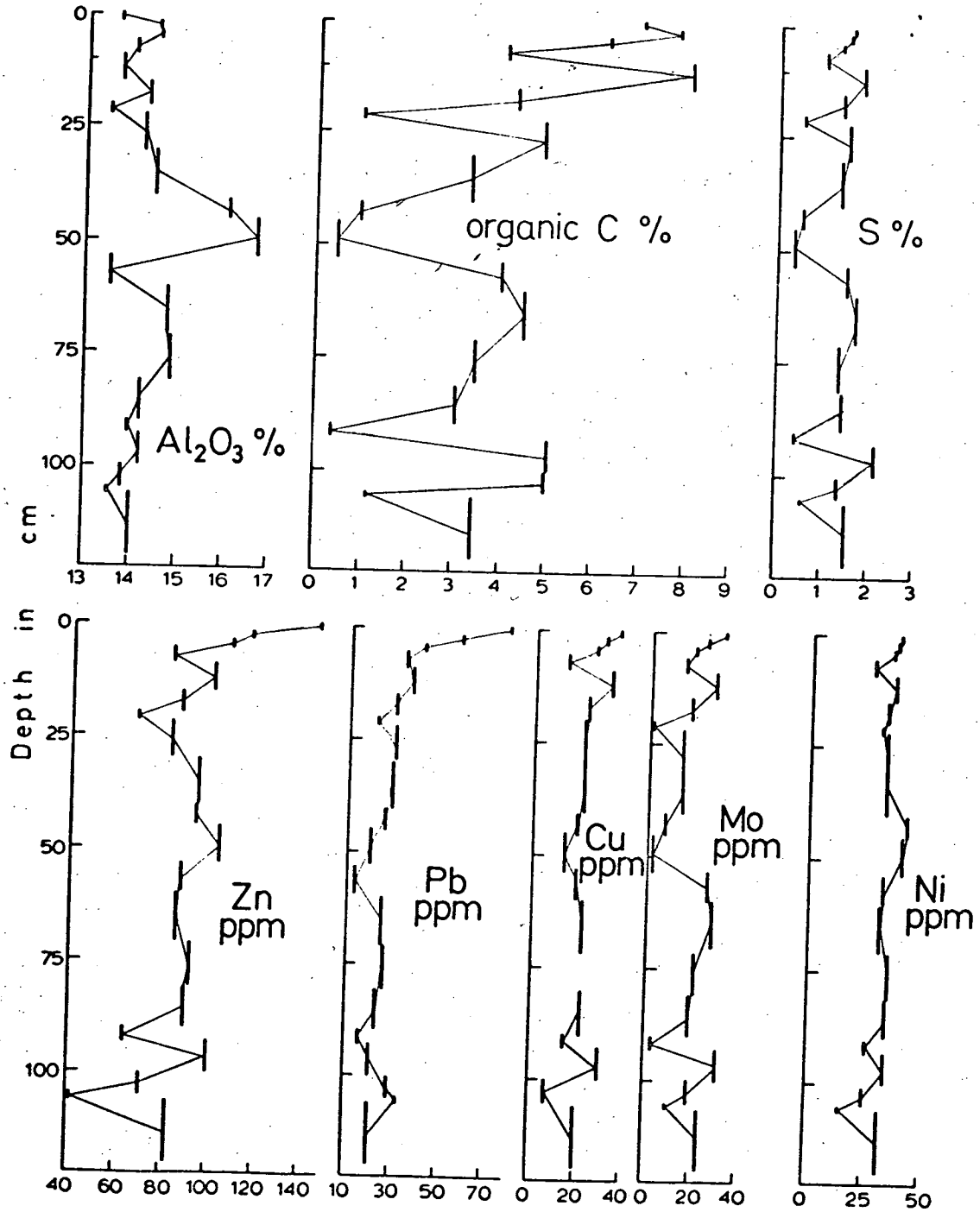


Fig. 6.12

Comparison of the vertical distributions of Zn, Pb, Cu, Ni and Mo with those of Al_2O_3, organic C and S in core Bo 6

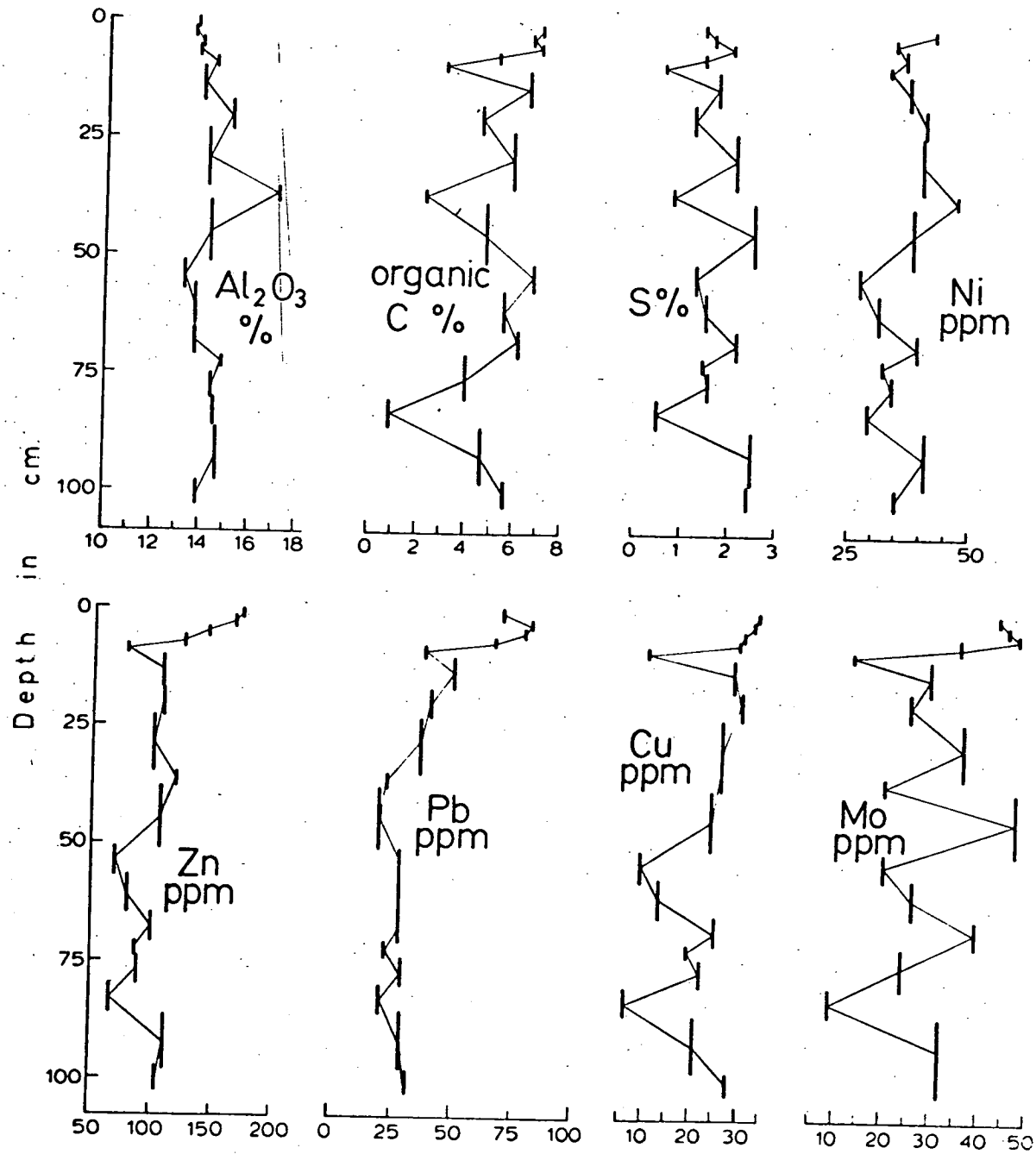


TABLE 6.10

Some element/Al_2O_3, element/organic C, and element/S ratios in the sediments

Core	Depth (m)	$\frac{Zn}{Al_2O_3}$	$\frac{Pb}{Al_2O_3}$	$\frac{Cu}{Al_2O_3}$	$\frac{Ni}{Al_2O_3}$	$\frac{Zn}{\text{organic C}}$	$\frac{Pb}{\text{organic C}}$	$\frac{Cu}{\text{organic C}}$	$\frac{Zn}{S}$	$\frac{Pb}{S}$	$\frac{Cu}{S}$	$\frac{Mo}{S}$
Anoxic sediments												
Bo 1	0-1.5	10.7	5.7	2.6	2.8	21	11.1	5.1	91	48	22	20
	1.5-3.5	8.1	4.0	2.1	2.6	15	7.5	3.9	77	38	20	16
	3.5-5.5	7.4	2.9	1.8	2.4	17	6.7	4.2	81	32	20	14
	5.5-9	5.9	2.4	1.0	1.9	21	8.4	3.5	82	34	14	15
	9-15	7.3	2.7	2.4	2.6	13	4.6	4.1	55	20	18	15
	15-20	6.1	2.1	1.6	2.3	20	7.0	5.3	63	22	17	13
	20-22	5.0	1.6	1.6	2.3	69	22.4	22.4	136	44	44	2
	22-30	5.8	2.1	1.5	2.3	17	6.1	4.5	56	20	15	10
	30-40.5	6.6	2.0	1.6	2.3	29	8.7	6.9	71	22	17	11
	40.5-45	5.8	1.6	1.2	2.6	100	27.7	20.2	184	51	37	14
	45-53.5	6.2	1.2	0.8	2.4	226	43.5	30.4	306	59	41	6
	53.5-60	6.5	1.0	1.4	2.4	22	3.3	4.8	60	9	13	18
	60-71	5.8	1.7	1.5	2.1	19	5.6	4.9	51	15	13	17
	71-81	6.2	1.8	1.6	2.4	27	7.5	6.6	70	20	18	16
	81-90	6.3	1.6	1.6	2.4	30	7.5	7.2	64	16	16	13
	90-93	4.6	1.1	1.1	1.9	168	42.1	39.5	168	42	39	8
	93-100	7.0	1.5	2.1	2.4	20	4.2	6.0	47	10	14	15
	100-105	5.1	2.1	0.5	1.8	14	5.8	1.4	52	21	5	14
	105-106	3.0	2.4	0.8	1.1	35	28.4	9.5	72	58	19	18
	106-120	5.9	1.5	1.4	2.3	24	6.1	5.8	55	14	13	16

Table 6.10 continued

Core	Depth (m)	Zn / Al_2O_3	Pb / Al_2O_3	Cu / Al_2O_3	Ni / Al_2O_3	Zn / organic C	Pb / organic C	Cu / organic C	Zn / S	Pb / S	Cu / S	Mo / S
Bo 6	0-2	12.6	5.0	2.4	3.1	25	10.0	4.8	124	50	24	31
	2-4	12.2	6.0	2.4	2.5	25	12.4	4.9	102	50	20	28
	4-6	10.4	5.6	2.2	2.6	21	11.3	4.3	72	39	15	24
	6-8	8.9	4.8	2.1	2.6	23	12.6	5.5	86	46	20	24
	8-10	5.3	2.5	0.7	2.3	26	12.3	3.3	133	64	17	22
	10-17	7.6	3.5	2.0	2.6	16	7.5	4.3	63	29	17	17
	17-23	7.1	2.6	2.0	2.7	23	8.6	6.4	89	33	25	20
	23-35	6.9	2.5	1.8	2.8	17	6.1	4.4	47	17	12	17
	35-38	6.9	1.3	1.5	2.7	52	9.6	11.4	151	28	33	25
	38-51	7.4	1.3	1.7	2.7	22	3.9	5.0	43	8	10	19
	51-57	5.3	2.1	0.7	2.0	10	4.1	1.3	54	21	7	15
	57-65	5.9	2.0	1.0	2.3	14	5.0	2.3	54	19	9	17
	65-71	7.3	2.0	1.8	2.8	16	4.5	4.0	46	13	12	18
	71-74	5.8	1.5	1.3	2.1	22	5.5	4.8	60	15	13	16
	74-80	6.1	2.0	1.5	2.3	22	7.2	5.5	56	18	14	15
	80-86	4.6	1.4	0.4	2.0	77	24.1	6.9	134	42	12	18
	86-98	7.6	2.0	1.4	2.8	24	6.1	4.4	46	12	9	13
	98-103	7.6	2.3	2.0	2.5	19	5.6	4.9	44	13	12	13
Mo 7(2)S	0-10	12.5	7.9	2.6	2.5	18	11.2	3.6	44	28	9	20
	10-20	8.1	3.5	1.6	2.3	18	7.6	3.4	51	22	10	27
	20-30	8.1	2.7	2.0	2.3	17	5.7	4.1	40	13	10	28
	30-40	9.1	2.8	2.3	2.4	18	5.5	4.4	47	14	12	26
	40-50	8.0	2.3	1.8	2.2	21	5.9	4.7	49	14	11	27
	50-60	7.6	2.5	1.6	2.3	31	10.1	6.6	51	17	11	28
	60-70	7.5	1.8	1.3	2.1	20	4.8	3.5	43	10	8	26
	70-80	7.5	2.1	1.7	2.0	52	14.6	11.6	78	22	18	43
	80-90	7.1	2.3	1.7	2.0	27	9.0	6.4	50	16	12	32
	90-100	7.3	1.3	1.5	2.0	31	5.5	6.2	48	9	10	24
	100-110	7.7	1.6	1.5	2.1	27	5.6	5.3	49	10	10	31
	110-130	8.4	1.7	2.1	2.4	19	3.8	4.7	40	8	10	23

Table 6.10 continued

Core	Depth (m)	$\frac{Zn}{Al_2O_3}$	$\frac{Pb}{Al_2O_3}$	$\frac{Cu}{Al_2O_3}$	$\frac{Ni}{Al_2O_3}$	$\frac{Zn}{organic\ C}$	$\frac{Pb}{organic\ C}$	$\frac{Cu}{organic\ C}$	$\frac{Zn}{S}$	$\frac{Pb}{S}$	$\frac{Cu}{S}$	$\frac{Mo}{S}$
Mo 26	0-5	14.2	9.0	3.1	3.0	16	10.2	3.5	143	91	31	27
	5-10	5.9	3.1	1.4	2.0	11	5.8	2.5	97	51	22	27
	10-15	9.0	4.0	2.3	2.6	13	5.8	3.4	85	37	21	30
	15-20	9.0	2.5	2.4	2.5	16	4.3	4.1	89	25	24	25
	20-25	8.4	2.5	2.3	2.8	14	4.1	3.7	74	22	20	26
	25-30	8.0	3.2	2.3	2.5	15	5.9	4.2	77	31	22	21
	30-35	6.6	2.1	1.6	2.2	16	5.1	4.0	68	21	17	23
	35-40	8.3	2.0	2.2	2.6	16	3.9	4.2	75	18	20	25
	40-45	9.2	2.1	2.3	3.1	16	3.7	4.1	63	14	15	23
	45-50	11.3	2.7	2.9	3.5	15	3.6	3.9	68	16	18	20
	50-55	8.7	2.0	2.1	2.5	23	5.3	5.6	77	18	19	19
	55-60	9.6	1.6	2.3	2.5	26	4.3	6.0	89	15	21	20
	60-65	7.7	1.8	2.0	2.4	23	5.6	6.2	88	21	23	24
	65-70	4.7	1.4	1.2	1.8	2.4	7.3	6.3	52	15	13	23
	70-75	7.3	1.9	2.0	2.5	16	4.1	4.3	46	12	12	22
Mo 34	0-3	15.2	5.6	3.0	3.2	29	10.7	5.6	73	27	14	43
	3-6	9.7	2.6	1.6	2.1	25	6.6	4.0	67	18	11	34
	6-8	8.4	1.8	2.4	3.4	14	2.9	3.9	39	8	11	38
Mo 10	0-5	5.2	3.3	1.2	1.8	13	8.4	3.1	149	96	35	59
	5-10	5.2	3.0	1.2	1.6	16	9.6	3.7	134	78	30	40
	10-15	5.6	3.7	1.0	1.5	23	14.8	3.9	250	163	43	40
	15-20	6.0	4.5	1.1	1.6	16	12.2	3.0	135	102	25	28
	20-25	4.5	2.9	1.1	1.5	15	9.5	3.5	112	73	27	31
	25-30	3.8	2.3	0.9	1.4	20	12.0	4.8	79	48	19	25
	30-35	3.5	2.2	0.6	1.4	15	9.5	2.4	63	39	10	40
	35-41.5	3.1	2.2	0.6	1.2	16	11.0	3.0	66	47	13	44

Table 6.10 continued

Core	Depth (m)	$\frac{Zn}{Al_2O_3}$	$\frac{Pb}{Al_2O_3}$	$\frac{Cu}{Al_2O_3}$	$\frac{Ni}{Al_2O_3}$	$\frac{Zn}{\text{organic C}}$	$\frac{Pb}{\text{organic C}}$	$\frac{Cu}{\text{organic C}}$	$\frac{Zn}{S}$	$\frac{Pb}{S}$	$\frac{Cu}{S}$	$\frac{Mo}{S}$
Oxic sediments												
Mo 22	0-2	10.6	4.5	2.1	2.4	50	22	10	1813	775	350	150
	2-4	10.1	4.0	2.0	2.3	48	19	9	1500	589	289	122
	4-6	8.9	3.5	1.6	2.2	45	18	8	946	369	169	46
	6-8	8.3	2.0	1.5	2.2	46	11	9	595	145	110	30
	8-10	8.0	2.2	1.3	2.1	54	15	9	688	188	112	47
	10-12	8.8	2.1	1.7	2.4	57	14	11	439	107	86	36
	12-14	9.1	2.2	1.8	2.4	59	15	12	610	150	120	55
Mo 42	0-2	10.0	3.6	1.8	2.4	69	25	12	1957	700	343	100
	2-4	8.5	3.5	1.6	2.2	51	21	9	1200	490	220	110
	4-6	7.6	1.6	1.3	2.2	63	13	11	514	109	91	164
	6-8	7.9	1.8	1.6	2.2	69	16	14	450	104	88	46
	8-10	8.0	1.4	1.3	2.2	68	12	11	460	80	76	44

All ratios have been multiplied by 10^4.

(Fig. 6.9-12) suggest that here the metals are not dominantly associated with either lithogenous matter, organic matter or sulphides. However the cause of the surface enrichments can be more closely pinpointed by careful examination of each of the possibilities. The presence or absence of Mn and Fe oxides in sediments of Osterfjord (p. 52) does not seem to influence the content of the trace metals. In addition the surface enrichments in the sediments from the inner basin of Bolstadfjord (Bo 1 and Bo 1A), where part of the water column is anoxic and hence where no oxides reach the sediment surface (p. 75), are just as great as elsewhere. Therefore it appears improbable that the high trace metal contents of the surface sediments are due to coprecipitation or adsorption by Fe(III) and Mn(IV) oxides. Coprecipitation or adsorption by sulphides is equally unlikely to be the main cause since surface enrichments occur irrespective of whether the sediments are oxic or anoxic and the metals would have to be almost totally excluded from the sulphides with burial in order to explain their rapid decrease with depth in the sediments. Thus only two likely explanations of the surface trace metal enrichments exist; they are a recent increase in the rate of deposition of the metals through pollution and/or a natural recycling process involving the deposition and burial of organically bound metals followed by their release during decomposition of the organic matter. The area has no likely source of metal pollution and there is no evidence of unusual concentrations of dissolved heavy metals in either the surface fjord waters or in rivers supplying the fjords (Appendix D). Therefore a natural recycling process of organically-

bound metals appears to be the most probable cause although its effect may be exaggerated by pollution. Doff (1970) observed a similar but greater heavy metal enrichment (Zn, Pb and Cu) in sediments of Oslofjord where it is probable that some heavy metal pollution does occur. In this instance the metal contents correlate with those of organic C in both oxic and anoxic surface sediments. The absence of such a correlation in the sediments examined in the present study may be due to the variability in composition of the organic matter (p. 54) and to a corresponding variation in its sorption capacity. For example the absence of any surface metal enrichment in core Mo 10 may be explained by a predominance of terrestrial organic matter. Since the metal/organic C ratios decrease with depth in many instances (see Table 6.10), it follows that the fraction of the organic matter holding much of the metals is altered more rapidly or to a greater extent than the main mass of organic matter.

There are several possible modes of origin of the organic matter-metal association. Living organisms, which are known to concentrate transition metals (Bowen, 1966), may be deposited after death along with their <u>in vivo</u> metal contents (Brongersma-Sanders, 1966). Alternatively adsorption of the metals may occur after death during settling of the organic detritus. The latter suggestion has been favoured to explain the metal enrichment in Oslofjord sediments since metal concentrations in living organisms are too small to account for the observed enrichments (Doff, 1970). However this is not a valid argument if a recycling process exists within the upper

few centimetres of sediment in view of the concept that a substantial proportion of the metals may be fixed near the sediment surface and hence will not reflect in vivo metal contents of the organic matter. Therefore the possibility that the metals are initially supplied to the sediment surface by settling-out of dead organisms containing only in vivo metal concentrations should not be excluded. In fact it is supported by combining two independent pieces of evidence. Firstly the observed metal enrichment occurs in the order Zn > Pb > Cu > Ni which is quite different from that of the relative stabilities of metal-amino acid complexes (Cu > Ni > Zn; Ahrens, 1966) and that of the sorption capacity of humate impregnated sands (Pb > Cu > Zn > Ni; Swanson et al., 1966). Secondly Zn and to a lesser extent Pb are concentrated more by plankton than are Cu and Ni (Bowen, 1966); dissolved Zn is in fact concentrated in the surface fjord waters, especially at the pycnocline (Appendix D), probably through its release from decomposing plankton (Sen Gupta, 1972). Finally it should be noted that trace metal concentrations in the source material will be an additional important factor in determining their relative degrees of enrichment in surface sediments. The average relative abundance of the relevant metals in granite is Zn > Pb > Cu > Ni (Krauskopf, 1967) which is the same as that observed in the sediments.

Mo concentrations are generally much higher in the anoxic sediments (1-119ppm) than in the oxic sediments (0-13ppm) and reflect an essential difference in the mode of Mo deposition in these contrasting environments although some superficial similarity does exist in this

respect. For instance Mo may be associated with lithogenous material (Krauskopf, 1956; Taylor, 1965) and organic matter (Krauskopf, op. cit.; Manskaya and Drozdova, 1968; also see p. 60) in both types of sediment. There is little evidence to suggest any other source of Mo in the oxic sediments including the possibility that the element is concentrated in Mn(IV) oxide rich sediments as in the deep sea (Bertine and Turekian, 1973) and possibly shallow water environments (see Berrang, 1972).

Mo enrichment in anoxic sediments is well documented (e.g. Kuroda and Sandell, 1954; Sugawara et al., 1961; Gross, 1967; Pilipchuk and Volkov, 1968; Crecelius, 1969; Doff, 1970; Presley et al., 1972) but its mode of incorporation has been argued over primarily as a result of the work of Krauskopf (1956) which suggests that sorption and organic reactions are the most likely mechanisms. A greater amount of observational and experimental evidence suggests that coprecipitation of Mo with iron monosulphides is more important (Sugawara et al., 1961; Pilipchuk and Volkov, 1968; Bertine, 1972). The contrasting Mo concentrations that exist between the oxic and anoxic sediments, and the high sub-surface as well as surface Mo contents in the anoxic sediments (Figs. 6.10-12) suggest that these high concentrations are related to sulphide precipitation (contrast to Pb, Zn and Cu; see p. 61). Unfortunately organic C contents are also generally high in the anoxic sediments relative to the oxic sediments so that a possible organic C-Mo relationship is not completely excluded by this evidence. However similar ranges of Mo and S concentrations to those observed in this study have been reported for

oxic and anoxic sediments from Oslofjord, but in contrast the organic C contents in the oxic sediments there (maximum >4.5% organic C) are almost as great as those in the anoxic sediments (Doff, 1970) indicating more clearly that Mo is mainly held in sulphides within the sediments.

The exceptionally low Mo concentrations in some sediment horizons in Bolstadfjord, particularly the coarse-grained and grey clay bands, are attributed to the correspondingly low S concentrations and hence to the rapid rate of deposition of the horizons (p.47). The two most important factors affecting the Mo/S ratio in anoxic sediments appear to be the variety of forms in which sulphur may be held in such sediments and the initial availability of Mo. The former is related not only to forms which may (e.g. iron sulphides) or may not (e.g. elemental S) contain Mo, but also to the different capacities that various iron sulphides found in sediments have for retaining Mo (Korolev, 1958; Bertine, 1972). The fact that Bolstadfjord sediments generally have much lower Mo/S ratios than the sediments of either Mofjord or Molviksfjord (Table 6.10) may reflect differences in these factors which result from the greater probable rate of deposition in Bolstadfjord (p. 46). For instance Berner (1964) states that the amount of pyrite relative to iron monosulphides is likely to increase with a decreasing sedimentation rate while it appears that Mo is not held to such a great extent by pyrite as it is by iron monosulphides (Korolev, 1958). With regard to the availability of Mo, Berrang (1972) has suggested that scavenging of the element by Mn oxides precipitating in the water

column followed by its release under anoxic conditions (see Chapter 7) provides a possible means of supplying Mo in sufficient quantities to explain its observed concentrations in anoxic sediments.

6.6 Possible Long-term Change in the Conditions of Sedimentation

Strøm (1936) suggests that the fjords of Norway have become increasingly anoxic as a result of post-glacial isostatic rebound. Doff (1970) also observed the onset of anoxic conditions in the sedimentary record of Oslofjord but attributed this mainly to unnatural eutrophication. Although it is not possible to contradict the overall interpretation of Strøm, it should be noted that certain observations on which his conclusions were based are invalid. For example Strøm (op. cit.) writes "There are several other cases where there is a sharp boundary between foul black sediments and underlying clays. The Mofjord, Bolstadfjord . . . sediments are examples of this. A change towards foul bottom waters is thus clearly indicated". The maximum length of Strøm's cores (43cm in Mofjord and 19cm in Bolstadfjord) were limited by the presence of stiff clay and sand horizons, and it is now known that such horizons occur irregularly with depth, particularly in Bolstadfjord, and are underlaid by normal anoxic sediment (p. 46 and Fig. 6.2).

There is virtually always a surface organic C maxima and an Al minima in the sediments (Fig. 6.13), but this may be due to either decomposition of a certain fraction of the organic matter in the upper part of the sediment column or decreasing input of lithogenic detritus with time rather than to increasing anoxicity. The only basin that appears to have undergone a significant long-term change

Profiles of Al_2O_3 and organic C in the longest core from each basin. (in wt.%)

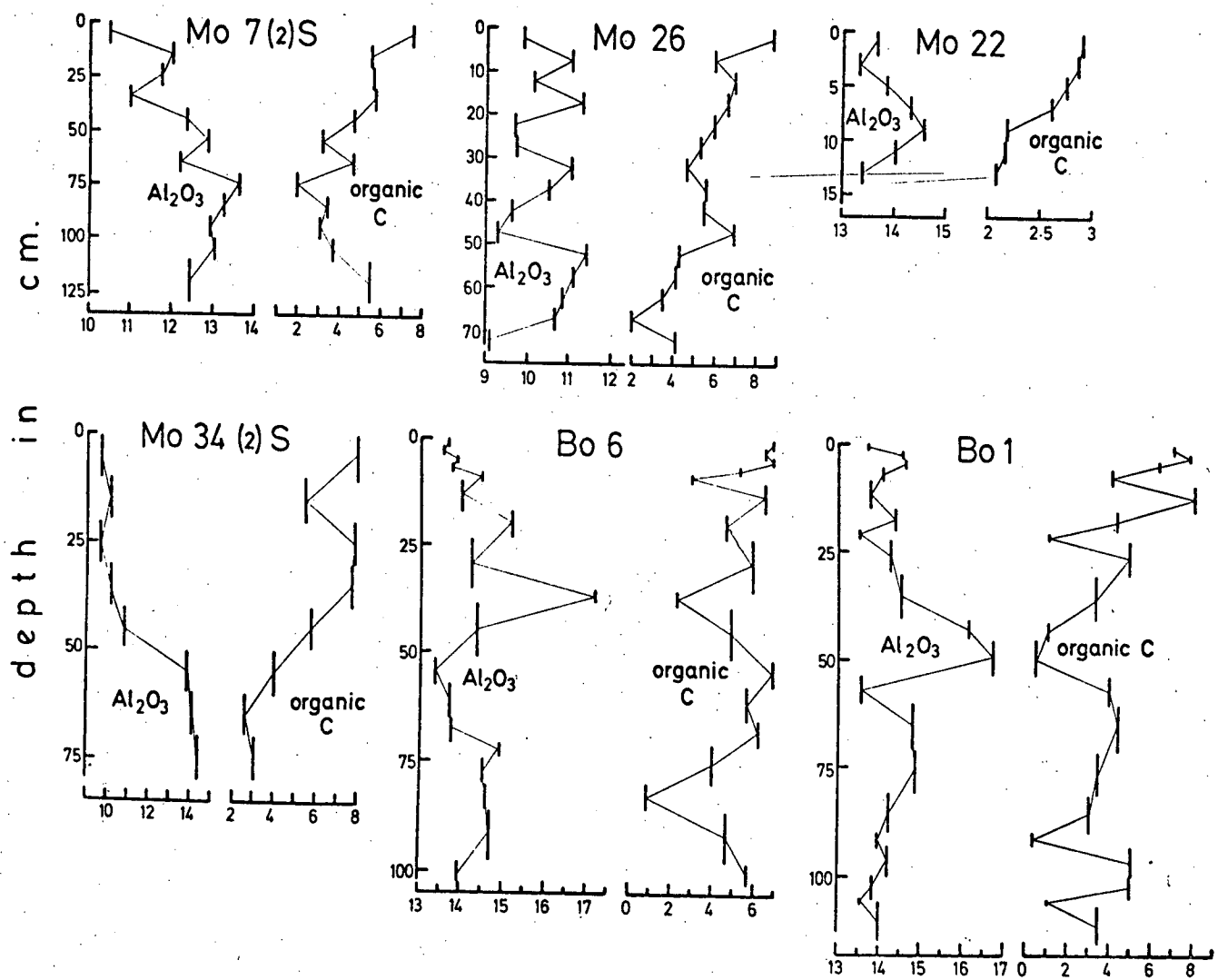


Fig. 6.13

Fig. 6.14

Vertical distribution of major elements in core Mo 34 (2) S. (in wt. %)

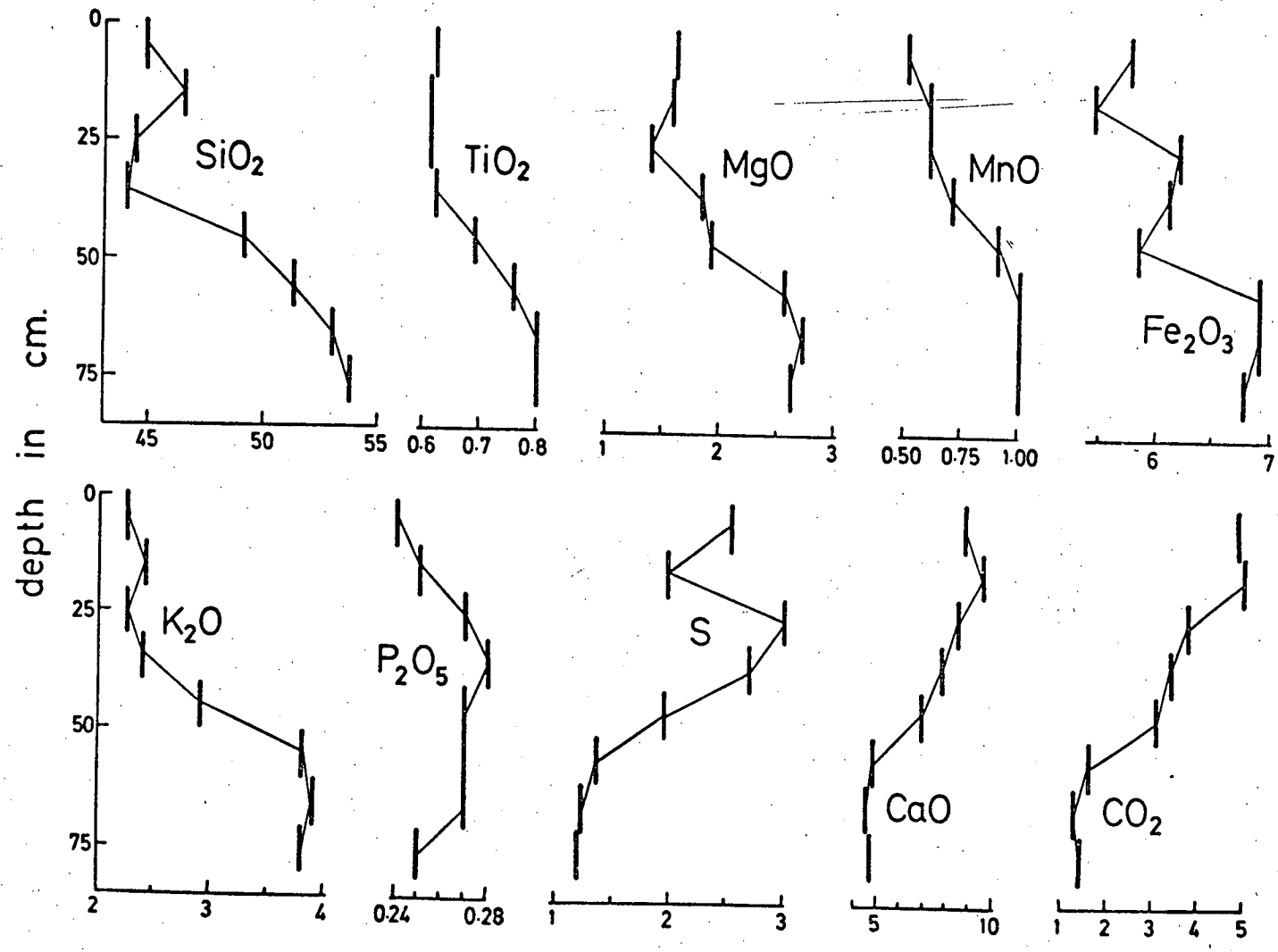
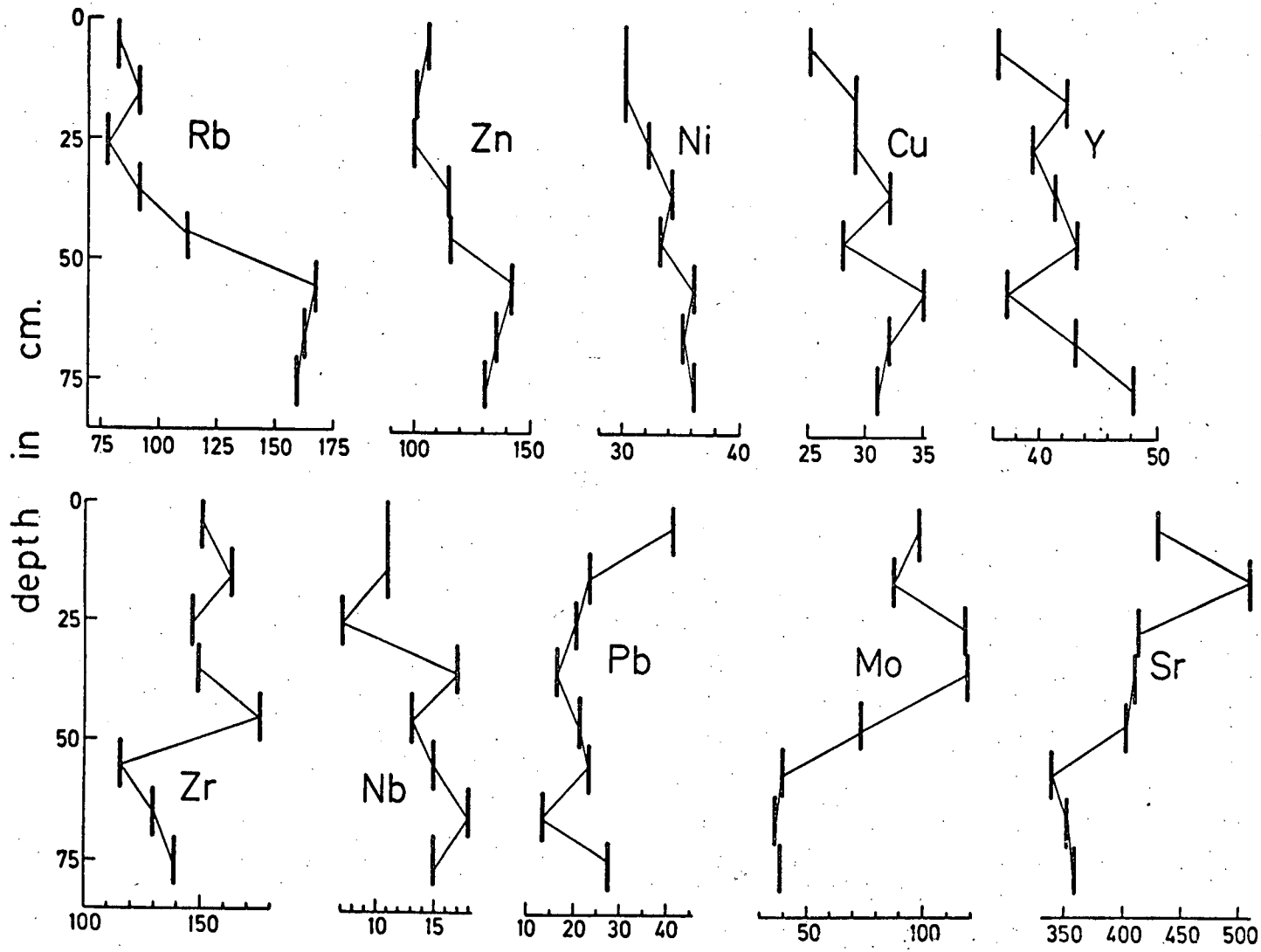


Fig. 6.15

Vertical distribution of trace elements in core Mo 34 (2) S. (in p.p.m.)



in its conditions of sedimentation is Holvikafjord. It was noted that a distinct break in lithology occurs between 40cm and 50cm (p. 46) and that this is reflected by certain element ratios (e.g. Zr/Rb, Zr/Al_2O_3) and the vertical distribution of the elements (Figs. 6.13,14 and 15). These changes, especially the marked increase in Mo, S and organic C contents, are taken to indicate an increase in the degree of anoxicity in the sediments with time although it is difficult to reconcile this with the observed increase in deposition of shell material (see Ca, CO_2 and Sr profiles in Figs. 6.14 and 15).

CHAPTER 7

IRON, MANGANESE AND RELATED ELEMENTS

7.1 Introduction

The water samples collected in 1970 and 1971 were analysed for dissolved as well as for particulate Fe and Mn. Interstitial water samples from five anoxic sediment cores (Mo 4(1)S, Mo 7(2)S, Mo 34(2)S, Bo 1A and Bo 2; see Fig. 6.1) were also collected during these two cruises. The dissolved metals from both the water column and interstitial waters were concentrated by a solvent extraction procedure prior to analysis by Atomic Absorption Spectrometry. Further details of water sampling and analytical procedures are included in Appendices A and C respectively, and a complete set of results in Appendix D. Owing to the precipitation of an Fe-rich phase in some interstitial water samples during storage (see Appendix A), only Mn concentrations are used in the following discussion.

7.2 The Distribution of Iron and Manganese in River and Surface Fjord Waters

Concentrations of dissolved Fe and Mn in the Rivers Vosso and Moelv are comparable to previously published data on river composition although their observed Fe contents are similar to the lowest values quoted (Table 7.1). The near-surface water concentrations of dissolved Fe and Mn are similar to the values reported from other fjords in Norway and British Columbia as well as to those in average sea water (Table 7.1). Relatively high concentrations of dissolved Fe

TABLE 7.1

Dissolved Fe and Mn concentrations in river and surface fjord waters (in µg/l)

River waters			Surface fjord waters		
	Mn	Fe		Mn	Fe
River Moelv 1970	3.1	5.6	C	<0.2-7.9	1.0-18.3
River Moelv 1971	2.7	5.2	D	20, 20, 20	5.0, 2.0, 15.8
River Vosso 1971	3.9	16.5	E	-	11-14
A	< 1-3*	< 10-710	F	2	10
B	7.0	670.0			

A 101 samples from surface waters of the Mackenzie River (Reeder et al., 1972).
* 99 of the 101 samples.

B Mn value is average world value for rivers suggested by Turekian (1969).
Fe value is average world value for rivers according to Livingstone (1963).

C 21 samples from 0-40m in Mofjord, Bolstadfjord and Osterfjord - this study.

D 3 samples from 0-20m in Saanich Inlet (Presley et al., 1972).

E 4 samples from 0-30m in Framvaren (Piper, 1971).

F Average sea water concentrations (Goldberg, 1965).

and Mn at Mo 23, Mo 49, Bo 1 and Bo 2 (Figs. 7.1-4) coincide, except at Mo 49, with that of suspended particulate matter (p. 34). There appear to be two or possibly three alternative mechanisms that may have caused such a feature. Firstly, as 'dissolved' ($<0.45\mu$) Fe and Mn are usually predominantly transported as colloidal material in rivers (Berner, 1970; Stumm and Morgan, 1970), a certain fraction of them may be precipitated when mixed with saline waters leaving high dissolved Fe and Mn contents in the overlying, fresher waters. Secondly, the decomposition of particulate organic matter concentrated at the pycnocline would result in a release of Mn and Fe (c.f. dissolved Zn maxima; p. 63) since both are concentrated by organisms, particularly diatoms (e.g. Vinogradova and Koval'skiy, 1972).
A third factor which may either enhance or possibly produce by itself the high surface dissolved Fe and Mn contents, is the lack of mixing between the surface, low salinity waters and the saline, deeper waters. That is to say downward movement of colloidal and truly dissolved species entering the fjords would be minimised by the marked density stratification (pycnocline) in near-surface waters. The existence of colloidal or complexed Fe is supported by the occurrence of 'dissolved' Fe within the surface waters of Mofjord and Bolstadfjord in concantrations that exceed the theoretical solubility by more than two orders of magnitude (observed $\sim 10^{-6.7}$, calculated $\sim 10^{-9.5}$–$10^{-8.0}$; using ionisation constants for amorphous $Fe(OH)_3$ after Krauskopf, 1967).

There is a near-surface maximum of particulate Fe at Mo 23, Mo 49 and Bo 1 (Figs. 7.1, 7.2 and 7.3) which also coincides with that

Fig. 7.1

Profiles of particulate (○) and dissolved (●) Fe and Mn at Mo 23.

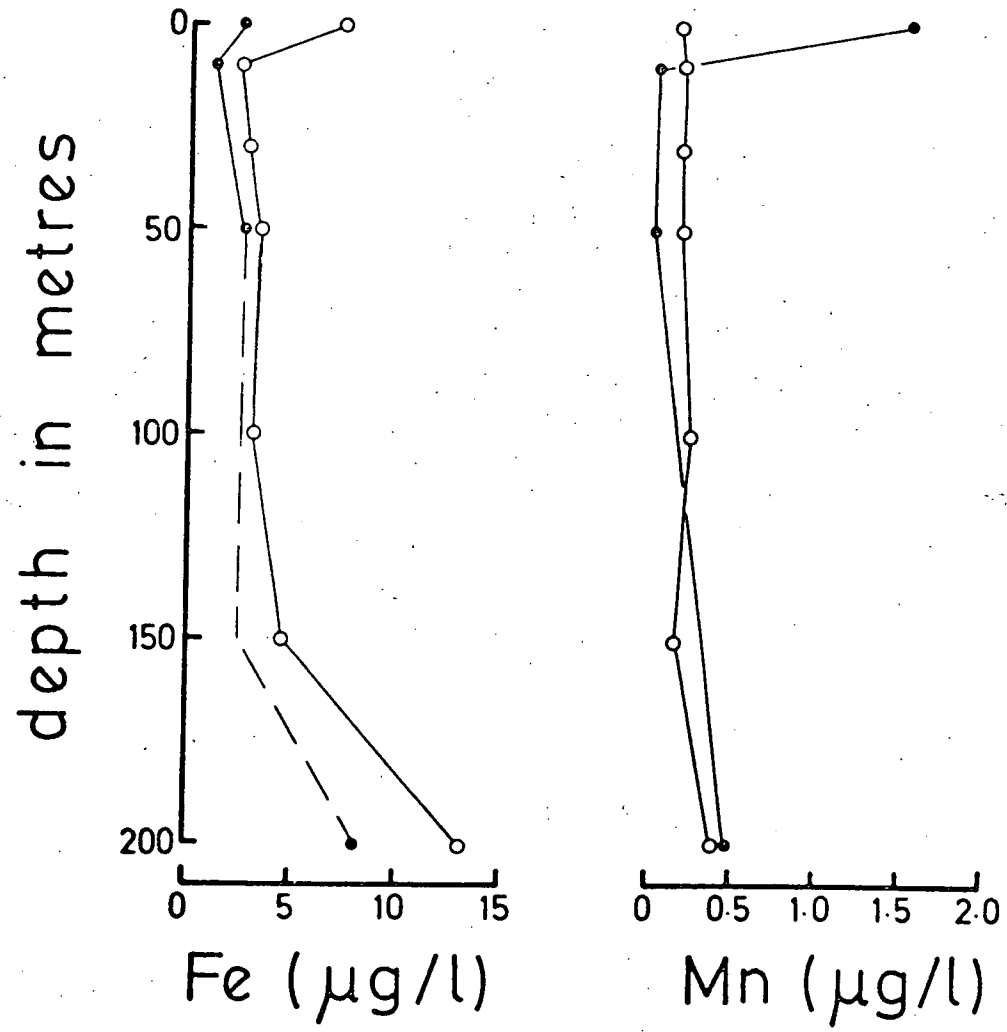


Fig. 7.2

Profiles of total (○) and excess (·) particulate Fe and Mn, dissolved (×) Fe and Mn, and total particulate P (▫) at Mo 49.

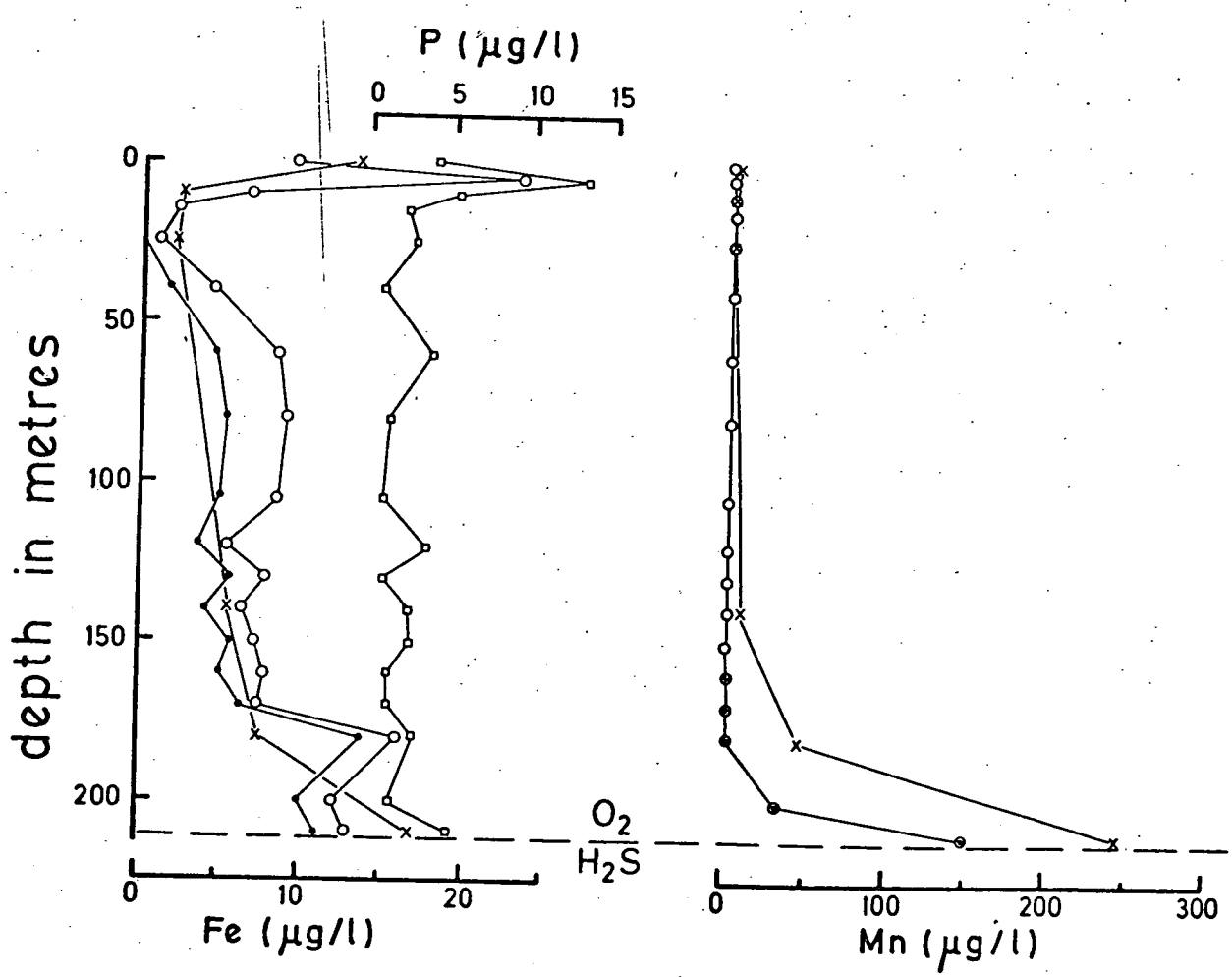


Fig. 7.3

Profiles of total (o) and excess (·) particulate Fe and Mn, dissolved (×) Fe and Mn, and total particulate P (▫) at Bo 1. (in µg/l)

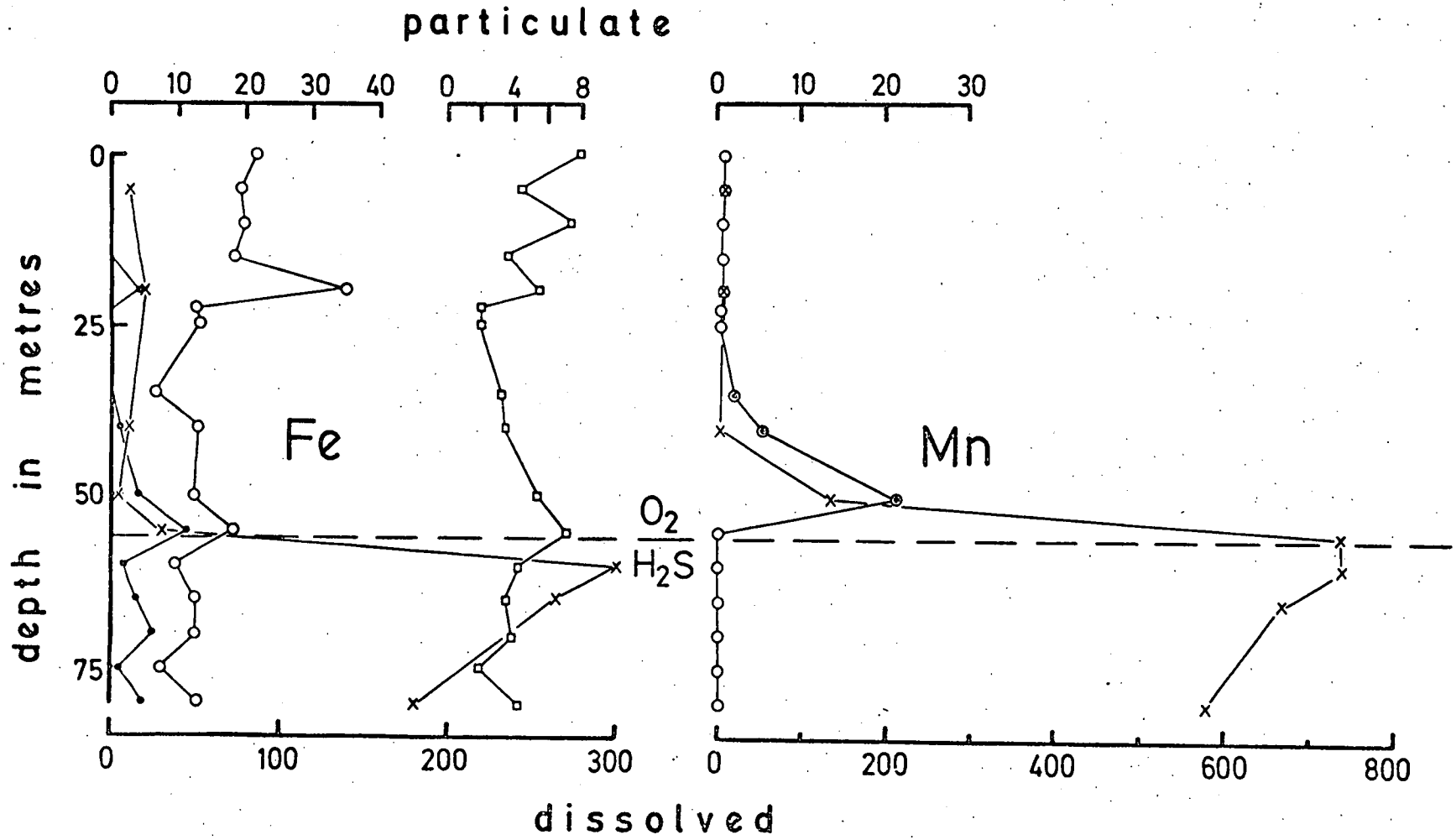


Fig. 7.4

Profiles of total (○) and excess (·) particulate Fe and Mn, dissolved (×) Fe and Mn, and total particulate P (○) at Bo 2.

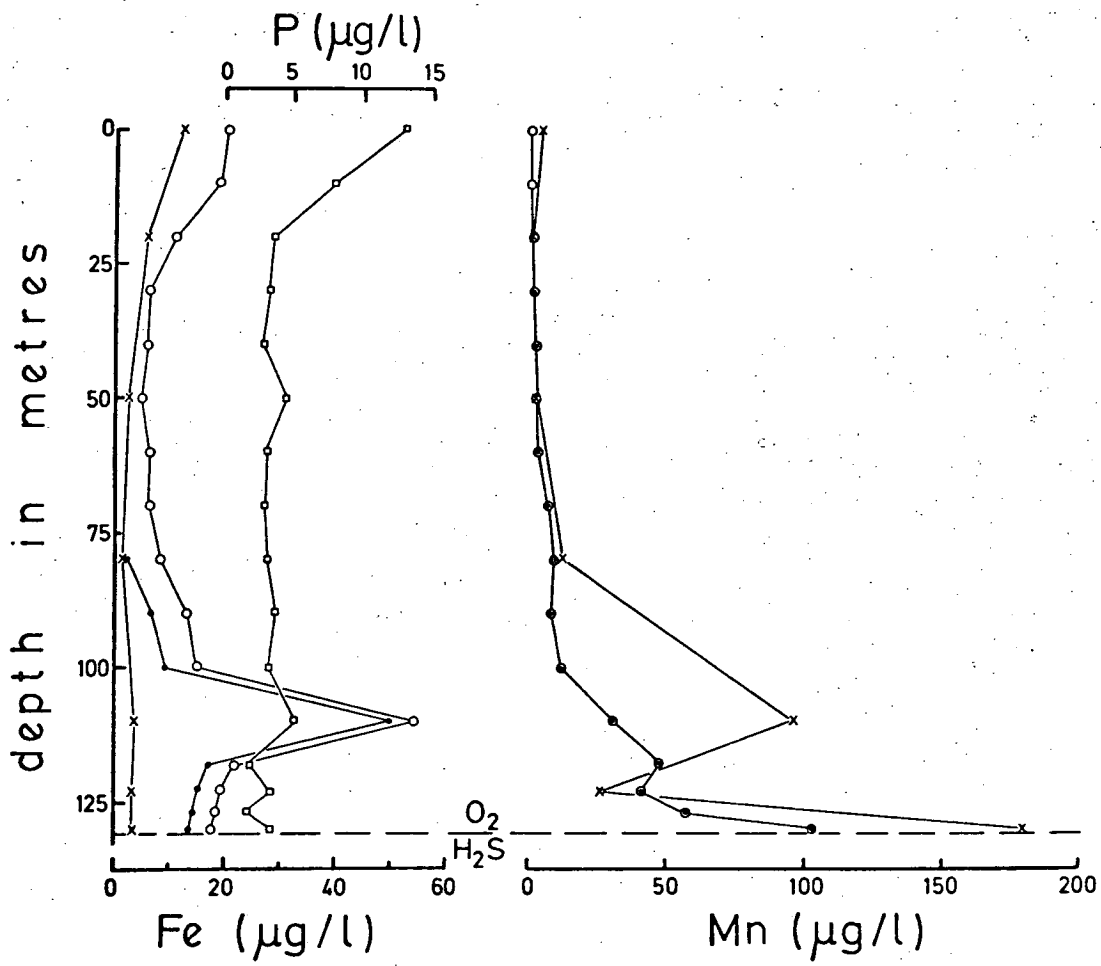
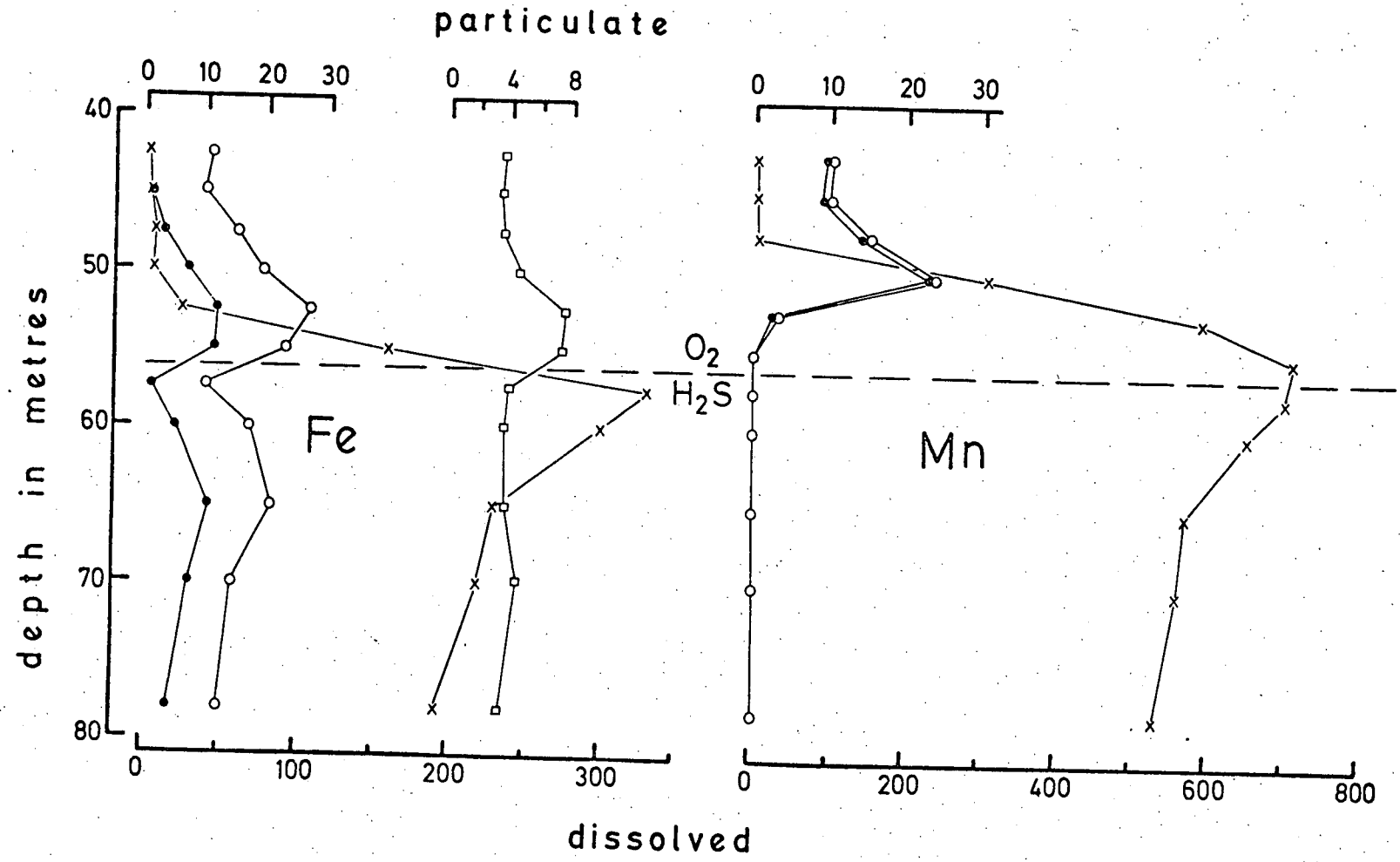


Fig. 7.5

Profiles of total (∘) and excess (·) particulate Fe and Mn, dissolved (×) Fe and Mn, and total particulate P (▫) at Bo 3. (in µg/l)



of inorganic particulate matter. The near-surface distribution of particulate Mn is similar except at Mo 23. Although these high values may be partly due to uptake of Fe and Mn by diatoms, the strong correlation between particulate Fe and Al in river and near-surface waters (Fig. 7.6) suggests that they are associated with the high aluminium-silicate contents. The most probable sites are within the lattice framework or as adsorbed ions associated with clay minerals and as oxide films on mineral grains (Carroll, 1958). The Fe/Al ratio (1.2) of the river and near-surface particulate matter is considerably higher than that of the bottom sediments (0.5-0.8) and will be used in the following discussion to estimate the amount of excess particulate Fe. Relatively rapid settling of non-Fe bearing aluminium-silicates (e.g. feldspars) and solution of surface oxide films under anoxic conditions may account for the low Fe/Al ratios of the bottom sediments.

7.3 The Distributions of Iron and Manganese in Sub-surface Fjord Waters

The distributions of both dissolved and particulate Fe and Mn vary greatly in sub-surface waters and can be related to the position of the O_2-H_2S boundary. Their description is therefore dealt with in three sections according to the relative position of this boundary.

a) O_2-H_2S boundary within the sediment column

There is a small increase in concentration of both dissolved and particulate Mn and Fe in the bottom waters compared to intermediate waters at Mo 23 (Fig. 7.1). The particulate Fe/Al (1.2) and Mn/Al (0.05) ratios however are constant throughout the water column (Table 7.2) indicating that the high bottom particulate Fe and Mn

Fig. 7.6

Fe-Al relationship in suspended particulate matter samples from Bo 1, Bo 2, Bo 3, Mo 23 and Mo 49

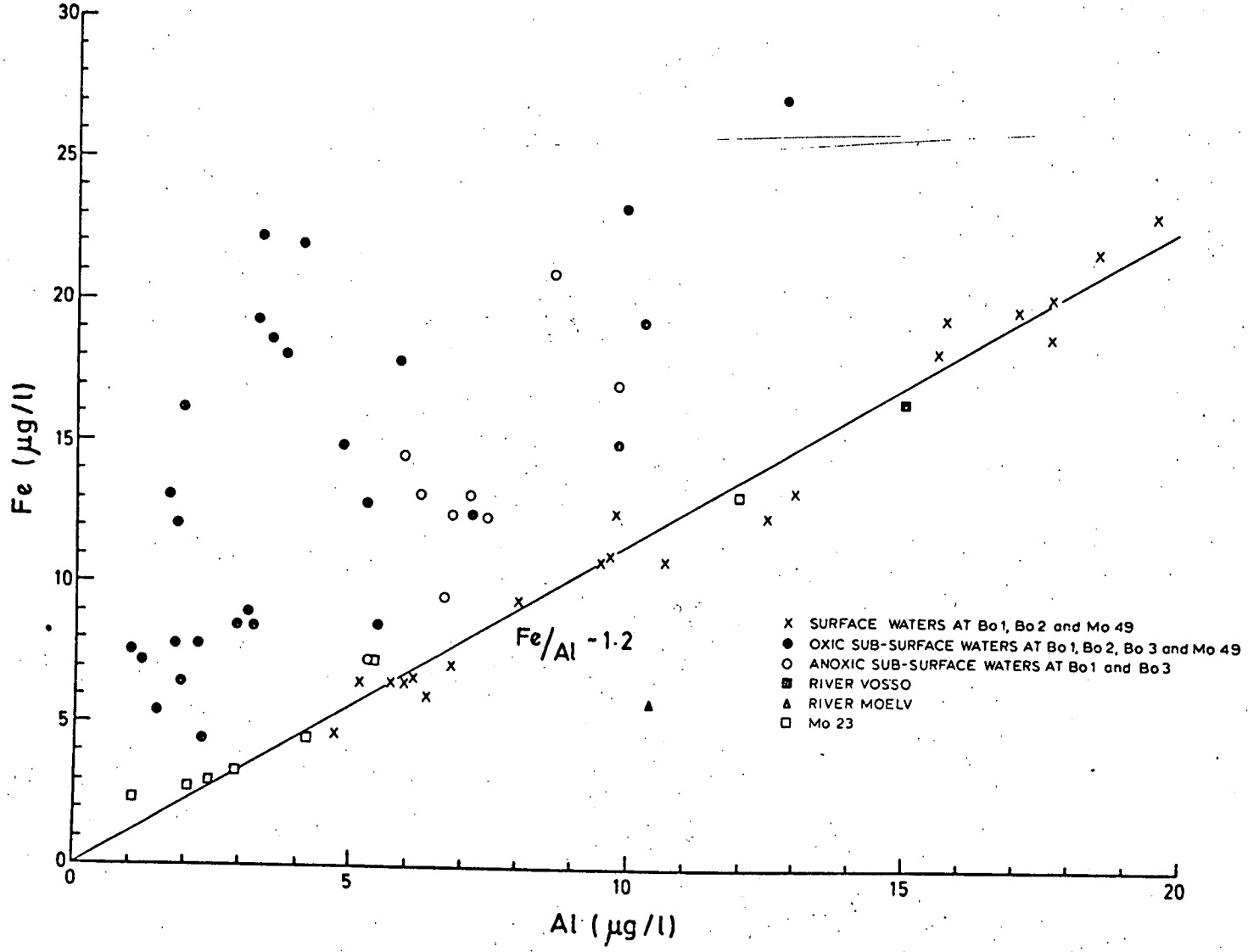


TABLE 7.2

Fe/Al and Mn/Al ratios in suspended particulate matter

Station	Depth (m)	Fe/Al	Mn/Al
Mo 23	0	1.38	0.023
1970	10	2.22	0.150
	30	1.38	0.085
	50	1.16	0.052
	100	1.26	0.109
	150	1.08	0.038
	20	1.08	0.036
bottom sediments			
at Mo 23		0.53	0.006
Mo 49	0	0.39	0.009
1971	0(2)	0.36	0.006
	2(2)	0.43	-
	5	1.19	0.030
	5(2)	1.15	0.038
	10	1.27	0.067
	10(2)	1.04	0.048
	15	-	0.060
	25	-	0.067
	40	1.92	0.76
	60	2.61	0.36
	80	2.89	0.10
	105	2.90	0.23
	120	3.57	0.44
	130	4.37	0.59
	140	3.40	0.92
	150	6.09	0.61
	160	3.50	1.01
	170	7.54	2.23
	180	8.36	1.04
	200	6.66	18.6
	210	7.90	90.7
bottom sediments			
at Mo 49		0.70	0.012
River Moelv		0.56	0.006
1971			
Bo 3	42.5	1.15	1.07
1971	45	1.18	1.23
	47.5	1.52	1.56
	50	1.88	2.33
	52.5	2.12	0.25
	55	2.35	0.016
	57.5	1.39	0.003
	60	1.74	0.009
	65	2.43	0.020
	70	2.45	0.008
	78	1.82	0.006
River Vosso		1.17	0.064
1971			

Station	Depth (m)	Fe/Al	Mn/Al
Bo 1	0	1.18	0.062
1971	5	1.16	0.051
	10	1.23	0.052
	15	1.18	0.054
	20	1.38	0.063
	22.5	0.99	0.065
	25	1.03	0.078
	30	-	-
	35	-	0.37
	40	1.29	0.69
	50	1.73	3.06
	55	3.07	0.026
	60	1.43	0.011
	65	1.66	0.009
	70	2.12	0.011
	75	1.35	-
	80	1.85	0.017
bottom sediments			
at Bo 1		0.74	0.010
Bo 2	0	1.15	0.039
1971	10	1.07	0.044
	20	1.20	0.091
	30	1.10	0.26
	40	0.94	0.39
	50	1.00	0.47
	60	1.09	0.55
	70	1.15	1.22
	80	1.54	1.69
	90	2.45	1.54
	100	3.08	2.47
	110	13.72	7.66
	118	5.41	11.7
	123	5.88	12.4
	127	5.28	16.2
	130	4.76	27.4
bottom sediments			
at Bo 2		0.59	0.010

contents are related to the probable resuspension of underlying sediments at this station (p. 36).

b) O_2-H_2S boundary at the sediment-water interface

The deep waters at Mo 49 and Bo 2 are greatly enriched in dissolved and particulate Mn relative to surface waters and show concentrations of up to 245µg/l and 149µg/l respectively (Figs. 7.2 and 7.4). In contrast to the situation at Mo 23 the deep water particulate Mn contents are also very high relative to particulate Al (Table 7.2). Both dissolved and particulate Mn concentrations increase exponentially with depth to the sediment-water interface. High concentrations of non-silicate particulate Mn (assuming a Mn/Al ratio of 0.05 for particulate silicates) are restricted to the bottom 10-20m of the water column at Mo 49, a poorly mixed zone of water (p. 15), whereas significantly high concentrations exist almost to the base of the pycnocline (27m) at Bo 2 (Figs. 7.2 and 7.4). To a lesser degree a similar relationship between dissolved Mn and water depth exists in these two profiles.

Concentrations of particulate Fe are also high in the sub-surface waters relative to both surface waters and particulate Al at these stations (Figs. 7.2 and 7.4, Table 7.2). However the enrichment of Fe is not as great as for particulate Mn (maximum particulate Fe = 54.6µg/l). In comparison dissolved Fe concentrations show little change between near-surface (0-25m) and deeper waters although at Mo 49 some increase with depth is observed. Two further features of the particulate Fe distribution are worth noting. These are the occurrence of a maximum some 20-30m above the sediment-water interface

in both profiles and the presence of a high, apparently non-silicate (i.e. excess) particulate Fe concentration throughout the sub-surface waters of Mo 49.

c) O_2-H_2S boundary within the water column

The profiles of dissolved Mn and Fe at Bo 1 and Bo 3 are similar to each other. Low concentrations, comparable with those in the surface waters, occur at intermediate depths (~30-50m) while both stations display very pronounced mid-water maxima below which dissolved Mn and Fe contents decrease somewhat (Figs. 7.3 and 7.5). Maximum concentrations of dissolved Mn (740µg/l) and Fe (300µg/l) are greater than the values reported in similar circumstances for the Black Sea (Table 7.3). The relative enrichment of Mn in the deeper waters is greater than that of Fe. Significantly the mid-water maximum of dissolved Mn occurs between 52.5m and 55m, about 2.5m above that of the maximum concentration of dissolved Fe. At these two stations the O_2-H_2S boundary occurs close to 55m depth.

The highest concentrations of particulate Fe and Mn occur in the mid-waters some 2.5-5m above the corresponding maxima of dissolved Fe and Mn (Figs. 7.3 and 7.5). The maximum values (particulate Mn = 23.8µg/l, particulate Fe = 23.2µg/l) are lower than those observed in the Black Sea (Table 7.3). A small, secondary high of particulate Fe is seen at 65-70m which is in contrast to the very low particulate Mn concentrations (not exceeding 0.2µg/l) below the O_2-H_2S boundary.

TABLE 7.3

Concentrations of dissolved and particulate Fe and Mn in anoxic basins

Location	Fe		Mn	
	dissolved	particulate	dissolved	particulate
Inner basin of Bolstadfjord	1.6-330	7.16-34.81	1.7-740	0.02-23.83
Black Sea[1]	0-20	4-102		
Black Sea[2]			0-495	0-280
Black Sea[3]	< 1-45	0.50-69.43	< 1-450	0.01-57.88
Saanich Inlet[4]	1.3-15.8		20-340	
Framvaren[5]	8.1-15	4.8-23		

1. Dobrzhanskaya and Pshenina (1959). (in µg/l)
2. Mokyevskaya (1961). (in µg/l)
3. particulate Fe and Mn from Spencer et al. (1972). (in µg/kg)
   dissolved Fe and Mn from Spencer and Brewer (1971). (in µg/l)
4. Presley et al. (1972). (in ppb)
5. Piper (1971). (in ppb)

7.4 The Distribution of Dissolved Manganese in Interstitial Waters

The concentration of dissolved Mn in anoxic interstitial waters is greater than in average sea water, in some instances by several orders of magnitude (Table 7.4). The highest values (maximum 12.3mg/l) occur in core Bo 2 where a Mn carbonate is suspected in the sediments especially below 40cm (p. 53). In core Bo 2A from the same location, a Mn carbonate probably exists at all depths in the sediment. There is no obvious relationship between the concentration of Mn in sediment interstitial waters and that found in the sediments. Respective values for interstitial Mn in Mn carbonate bearing and other anoxic sediments from Saanich Inlet (Presley et al., 1972) and in Mn carbonate bearing sediments from Loch Fyne (Calvert and Price, 1972) are similar to those observed in this study. In cores Mo 7(2)S, Bo 1A and Bo 2, interstitial Mn contents decrease rapidly with depth (Table 7.4 and Fig. 7.7).

7.5 Phase Transformations of Iron and Manganese

In contrast to the high particulate Fe and Mn contents in the bottom waters of Osterfjord (Mo 23), those in the sub-surface waters of Mofjord and Bolstadfjord do not relate to particulate Al concentrations and hence must represent authigenic non-silicate phases. Their presence in the bottom waters at Mo 49 and Bo 2 partly accounts for the observed high concentrations of total suspended particulate matter (p. 34).

From the preceding description of changes of dissolved and particulate Mn in various profiles some relationship between their

TABLE 7.4

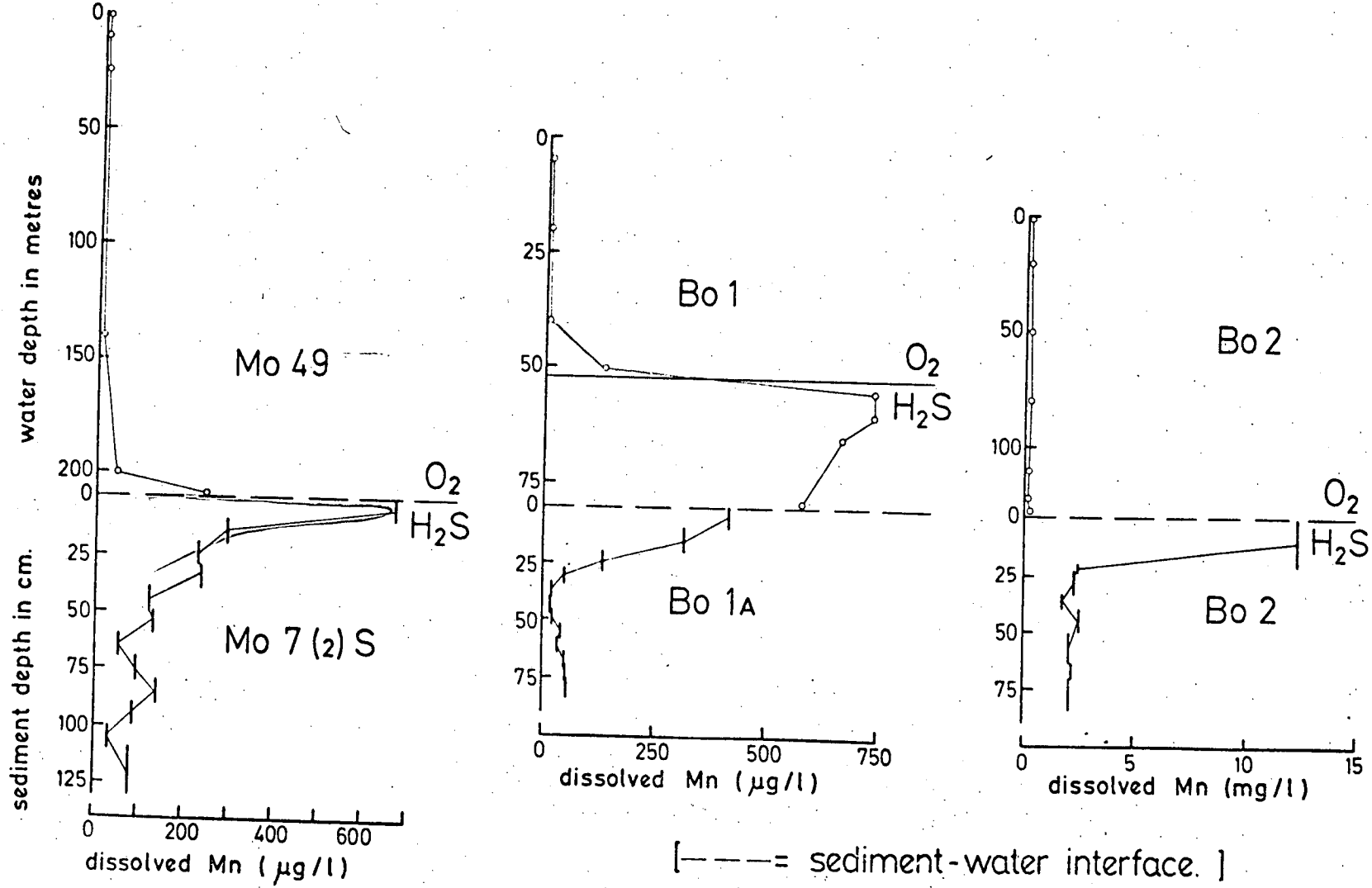
Dissolved Mn concentrations in interstitial waters (in µg/l)

Core	Depth (m)	Mn
Mo 4(1)S 1970	0-10	45
	10-20	439
	20-30	96
	30-40	66
	40-50	38
	50-60	25
	60-70	16
	70-80	21
Mo 7(2)S 1970	0-10	671
	10-20	292
	20-30	231
	30-40	236
	40-50	121
	50-60	130
	60-70	55
	70-80	92
	80-90	137
	90-100	86
	100-110	33
	110-130	80
Average seawater (Goldberg, 1965)		2

Core	Depth (m)	Mn
Mo 34(2)S 1970	0-10	37
	10-20	48
	20-30	45
	30-40	38
	40-50	70
	50-60	37
	60-70	26
	70-80	16
Bo 1A 1971	0-10	418
	10-20	317
	20-27	136
	27-34	49
	34-39	21
	39-46	20
	46-52	22
	52-58	41
	58-64	38
	64-71	51
	71-76	52
	76-82	54
Bo 2 1971	0-21	12278
	21-24	2445
	24-34	2358
	34-40	1755
	40-50	2555
	50-63	2064
	63-70	2205
	70-83	2187

Fig. 7.7

Vertical distribution of dissolved Mn in interstitial waters and the overlying water column.



[———= sediment-water interface.]

trend and the position of the O_2-H_2S boundary is manifest. Relatively large dissolved and very small particulate concentrations of Mn occur below this boundary except at Bo 2/Bo 2A where Mn carbonate exists in the sediment. In contrast low dissolved and high particulate Mn concentrations are observed above the boundary. The same trends in Fe can be observed where the O_2-H_2S interface occurs in the water column but cannot be confirmed where the interface occurs at the sediment surface due to the absence of interstitial Fe data.

Assuming reactions between solid and dissolved phases of both metals actually occur, it is evident from the profiles at Bo 1 and Bo 3 that these transformations do not coincide exactly with the O_2-H_2S boundary and are independent of each other. That involving Mn occurs some 2.5m above that for Fe which takes place immediately above the O_2-H_2S interface. This distinction between the Mn and Fe reactions is probably a reflection of differences in pE values[1] for the respective redox couples e.g. (after Stumm and Morgan, 1970):-

$$Fe(OH)_3(S) + 3H^+ + e = Fe^{2+} + 3H_2O \qquad pE^o = +18.8$$

$$\tfrac{1}{2}MnO_2(S) + 2H^+ + e = \tfrac{1}{2}Mn^{2+} + H_2O \qquad pE^o = +21.0$$

The assumption that so-called 'particulate' and 'dissolved' Mn and

---

1 For half cell reaction:- $ox + ne^- = red$

$$\log K = \log a_{red} - \log a_{ox} + npE$$

where ox = oxidised species, red = reduced species, n = number of electrons transferred, and a = activity.

$$pE = pE^o + \frac{1}{n} \cdot \log\left(\frac{a_{ox}}{a_{red}}\right), \quad \text{where } pE^o = \frac{1}{n} \cdot \log K$$

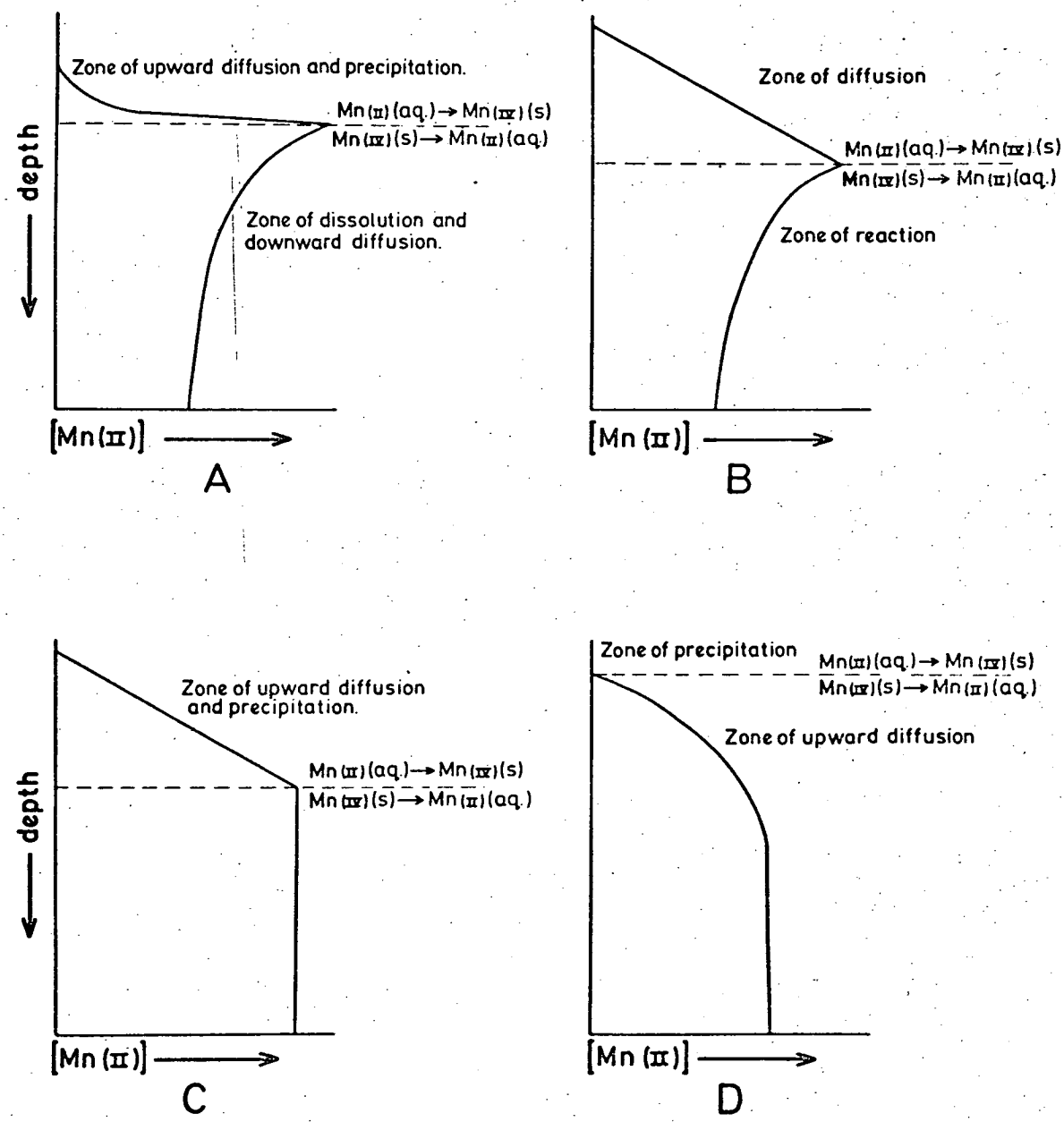
when all species other than electrons are at unit activity.

Fe truly represent insoluble Mn(IV), Fe(III) phases and soluble divalent species respectively, is reasonable since it has been shown to be the case for Mn in a study of lake waters (Delfino and Lee, 1968).

Similar changes of dissolved and particulate Fe and Mn occur across the O_2-H_2S boundary in the Black Sea (Spencer and Brewer, 1971; Spencer et al., 1972) and in some lakes (Hutchinson, 1957). Spencer and Brewer (op. cit.) have interpreted the distribution of particulate and dissolved Fe and Mn in the Black Sea in terms of redox reactions and vertical advection-diffusion processes. That is, descending particulate Fe(III) and Mn(IV) oxides-hydroxides are reduced and solubilised to Fe(II) and Mn(II) at the appropriate redox (pE) boundaries consequently establishing a reservoir of Fe(II) and Mn(II) below. Upward movement of part of this reservoir through vertical advection and diffusion, and subsequent oxidation re-precipitates the metals as Fe(III) and Mn(IV) phases at or above their respective redox boundaries. This cyclic process is capable of maintaining the mid-water maxima of both dissolved and particulate Mn and Fe as long as both metals are continually supplied from surface waters. A similar model can be applied to the Mn and Fe profiles at Bo 1 and Bo 3 (see A, Fig. 7.8). The major departure from Spencer and Brewer's (1971) model is that, unlike the Black Sea where a deep and rather constant advective inflow through the Bosphorus occurs, renewal of bottom waters in the inner basin of Bolstadfjord is probably intermittent and rapid (see section 3.7). As a consequence the Mn and Fe profiles are probably maintained by diffusion

Fig. 7.8

Idealised dissolved Mn profiles



processes for the most part with advection being significant only at irregular time intervals. Unfortunately quantitative treatment of the data is made impossible by a lack of detailed knowledge concerning the circulation in the basin and the probable absence of steady state conditions in the water column or even an approach towards them.

A consequence of the model described above is that the overall concentration of both elements in the reservoir (the anoxic waters) will increase. This build-up of Mn and Fe may be limited by physical processes (e.g. transport of Mn and Fe out of the basin), by chemical processes (e.g. in situ precipitation of a divalent solid phase) or by a combination of the two. At Bo 1 and Bo 3 the excess particulate Fe occurring below the Fe(III)-Fe(II) redox boundary probably represents precipitation of a Fe(II) sulphide. No such buffering of the Mn(II) content occurs and explains why dissolved Mn is enrichod relative to Fe in the water column. Fig. 7.7 shows that the dissolved Mn concentration continues to decrease gradually with depth even within the surface sediments indicating that the sediment and water columns may be considered as one uninterrupted profile. Therefore the high surface interstitial Mn concentrations are probably the result of downward diffusion of Mn(II) from the water column particularly as no Mn(IV) solid phases can reach the sediment surface.

The Mn profile at the deep station in Mofjord (water station Mo 49 and core Mo 7(2)S), where the O_2-H_2S boundary occurs at or very close to the sediment-water interface, seems to be directly analogous

to that within the inner basin of Bolstadfjord (Bo 1 and Bo 3). That is, the maximum concentration of dissolved Mn occurs directly below the redox boundary (Fig. 7.7) while the highest particulate Mn contents exist directly above (Fig. 7.2). At the same time no Mn(II)(S) phase appears to be precipitating below this interface (i.e. in the sediments; see p. 51) where the concentration of dissolved Mn decreases with depth (Fig. 7.7). As at Bo 1 and Bo 3 upward diffusion of Mn(II) across the Mn(II)-Mn(IV) redox boundary and its subsequent oxidation probably causes the observed precipitation of Mn presumably as Mn(IV) oxides-hydroxides. With regard to the interstitial Mn profile however, it is apparent that the situation is not directly comparable to that at Bo 1 and Bo 3. Namely the O_2-H_2S boundary, which in this case is coincident with the sediment-water interface, is probably migrating upwards with time relative to sea-level due to sedimentation (see Emery, 1960). This has interesting implications when it comes to explain the observed downward decrease of interstitial Mn contents if it is assumed that the latter feature reflects steady state conditions within the sediment (i.e. if the dissolved Mn maximum is permanently located directly beneath the sediment-water interface). In the first instance the decrease with depth may be due to the rapid reduction and dissolution of Mn at the sediment surface followed by its downward diffusion as Mn(II). Relative to the sediment-water interface however, the interstitial waters containing these high dissolved Mn contents would move downwards as sedimentation proceeds. Therefore another mechanism must be found that can maintain the

dissolved Mn maximum directly below the sediment surface. The upward advection of interstitial waters relative to a given sediment horizon, which results from compaction of a sediment (Emery, 1960), is the only process capable of fulfilling this requirement. A constant supply of Mn from surface fjord waters plus upward advection of Mn(II) rich interstitial waters will lead to an ever increasing dissolved Mn content in the surface sediments until a point in time is reached, given favourable conditions, when Mn(II) precipitation may be effected. All that has so far been discussed concerning the distribution of dissolved Mn in core Mo 7(2)S is consistent with the assumption that the sediment-water interface is rising due to deposition. If on the other hand the sediment being laid down is somehow accommodated at depth so that the sediment surface remains stationary relative to sea-level, it is not necessary to invoke advection of interstitial waters to explain the distribution of Mn. Instead an identical process to that occurring in the water column at Bo 1 and Bo 3 (see p. 75) is sufficient.

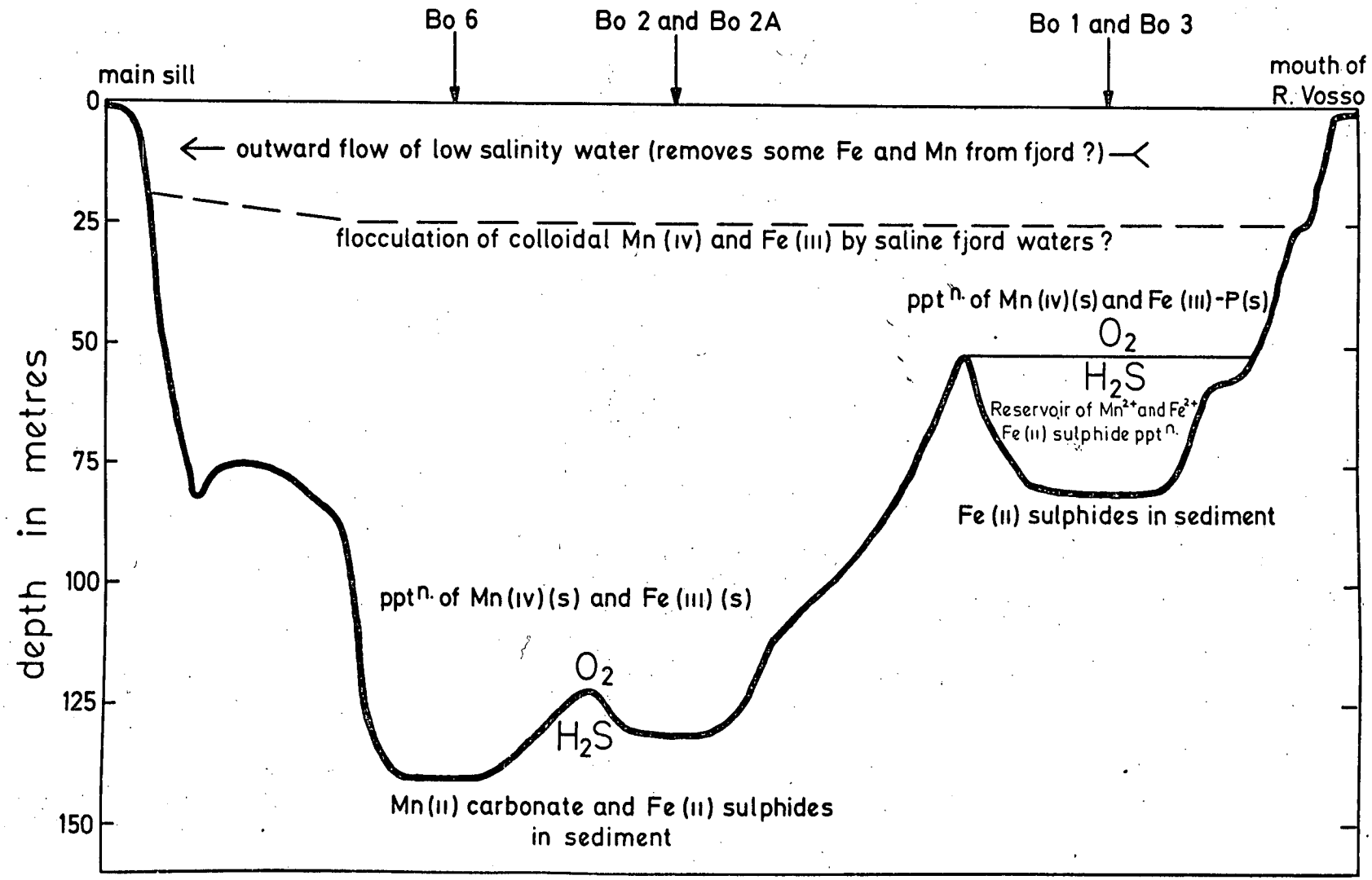
The mechanisms controlling interstitial Mn distribution, which were described above, are based on downward diffusion and/or upward advection, and therefore are very different from those described by Berner (1971) for anoxic sediments with thin oxide surface layers (see D, Fig. 7.8) and by Lynn and Bonatti (1965), Anikouchine (1967), and Bender (1971) for deep-sea sediments (see C, Fig. 7.8; after Bender, 1971). These models are all based predominantly on upward diffusion and are incompatible with the interstitial Mn profiles observed in this study.

At Bo 2 the distribution of Mn is again different in that a Mn(II) solid phase (a carbonate) probably exists below the Mn(IV)-Mn(II) redox boundary (i.e. below the sediment-water interface). Unlike core Bo 2A however there is no evidence in core Bo 2 that the carbonate has precipitated directly beneath the surface of sedimentation in the recent past. The shape of the dissolved Mn profile relative to the redox boundary is similar to those already described but the Mn contents are much greater (Fig. 7.7). The profile closely resembles that in sediments from Loch Fyne (Calvert and Price, 1972) where Mn carbonate seems to be precipitating at the present time. According to Calvert and Price (1972) the downward decrease in interstitial Mn is due to precipitation of the carbonate and to a downward exponentially decreasing production rate of dissolved Mn (due to a decreasing amount of Mn(IV) oxides-hydroxides) coupled with recycling of Mn(II) as a result of compaction (see B, Fig. 7.8). Interestingly these authors suggest that the latter mechanism, which is similar to one used to explain the distribution of Mn at Mo 49-Mo 7(2)S, could produce the same type of interstitial Mn profile even in the absence of carbonate precipitation. It seems more likely therefore that rather than causing the downward decrease in dissolved Mn, precipitation of carbonate is simply the natural consequence of the build-up of Mn(II) with time. In other words the decrease of interstitial Mn with depth existed prior to carbonate precipitation (as at Mo 49-Mo 7(2)S) which can only occur when Mn^{2+} activity is sufficient to exceed the carbonate's solubility product. It follows that precipitation is most likely to occur directly

beneath the Mn(IV)-Mn(II) boundary where the concentration of dissolved Mn(II) is greatest. However it is known that carbonate alkalinity in anoxic sediments generally increases with depth (Berner et al., 1970; Nissenbaum et al., 1972) so that Mn carbonate precipitation may occur well below the redox boundary due to increasing CO_3^{2-} activity. The difference between cores Bo 2 and Bo 2A, with regard to the presence or absence of Mn carbonate in the upper part of the sediment column, suggests that either interstitial Mn(II) concentrations vary laterally over short distances or that Mn(II) carbonate is not precipitating uniformly at the sediment surface.

A comparison of the amount of non-silicate Mn present within a column, having a 10 x 10cm cross-section and including the entire water column and the upper 100cm of sediment, shows that between two and three orders of magnitude more Mn occurs at Bo 2 (middle basin) than at Bo 1 (inner basin). It is reasonable to assume that this figure provides a minimum estimate of the true relative Mn distribution between the outer two basins and the inner basin of Bolstadfjord since it is known that Mn carbonate is also precipitating in the sediments of the outermost basin (see core Bo 6, p. 53) and the outer and middle basins combined are far larger in area and volume. The reasons for this unequal distribution become evident when the bathymetry of the fjord is examined in conjunction with its hydrochemical character (see Fig. 7.9). Most of the Mn entering the fjord probably does so via the River Vosso (p. 16). A proportion of it is immediately transported to the outer basins while the rest

Fig. 7.9 Idealised distribution of Fe and Mn in Bolstadfjord



is trapped within the inner basin. Most of the non-silicate fraction of the latter cannot reach the surface of sedimentation since it goes into solution in the anoxic waters below ~55m (see water stations Bo 1 and Bo 3). As Mn carbonate precipitation does not occur within the inner basin, non-silicate Mn can only be removed from there by its precipitation on that part of the basin floor occurring above the O_2-H_2S boundary or by its subsequent transport into the outer basins. Mn reaching these basins is either trapped there or removed from Bolstadfjord completely by surface outflow. The former is deposited on the sediment surface, which is at a greater depth (130-140m) than that within the inner basin (80m), and only then goes into solution as Mn(II) (see Bo 2). Thus the water column of the inner basin merely acts as a temporary reservoir of Mn (and Fe) whereas the outer two basins approximate an ultimate 'sink' for these metals. Hence the Mn content (mainly as Mn(II)) has built up to such an extent that Mn(II) carbonate is able to precipitate.

The only other cores (Mo 4(1)S and Mo 34(2)S) from which interstitial waters were sampled do not conform with those already discussed in that the dissolved Mn concentration is low throughout. In both instances the O_2-H_2S boundary occurs at the surface of sedimentation. It is fruitless to speculate about the origin of these two dissolved Mn profiles as there are several, equally plausible explanations for them. In the case of core Mo 4(1)S it is worth mentioning however that the reason for the observed profile may be related to the change in hydrochemical conditions within the water

column which accompanied the deepening of the sill (p.16).

The distributions of Fe and Mn have so far been interpreted using simple thermodynamic concepts and mixing processes. Certain features however can only be understood with some knowledge of the kinetics of Mn and Fe redox reactions. According to Stumm and Morgan (1970), the oxidation of Mn(II) is autocatalytic with respect to the Mn oxide precipitated and its rate increases with increasing pH. The deep waters of Mo 49 have a higher pH (7.24) as well as higher dissolved and particulate Mn concentrations than those at Bo 2 (pH = 6.65). Therefore the greater dispersion of Mn in the water column at Bo 2 (p. 71) can be at least partly attributed to a slower rate of oxidation irrespective of any differences in mixing between the two stations. In fact the hydrographic data indicates that the water column at Mo 49 is better mixed than at Bo 2 except possibly within the bottom ~15m. One unresolved problem however is the inconsistency between the oxidation rate of Mn(II) necessary to maintain the observed particulate and dissolved Mn profiles and that derived experimentally (see Spencer and Brewer, 1971). Dr. P. G. Brewer (pers. comm.) has suggested that bacterial processes may be important in catalysing this type of oxidation reaction in natural waters. The rate of Fe(II) oxidation is significantly faster than that of Mn(II) but also increases with increasing pH (Stumm and Morgan, 1970). The relatively rapid rate of Fe(II) oxidation may explain why, in the deep waters at Mo 49 and Bo 2 (p. 71), the concentration of particulate Fe is greater than that of dissolved Fe while the reverse is true for Mn. It also implies that the high

particulate Fe content in the sub-surface waters at Mo 49, in contrast to particulate Mn, cannot be due to Fe(II) diffusing out of the underlying sediment. Instead this Fe is most probably supplied from surface waters through precipitation of colloidal Fe(III) (p. 69).

In Chapter 4 the observed pE values of the waters at Bo 1 were compared with those calculated using three possible pE controlling reactions without much success. The major change in pE at this station occurs between 50m and 65m (Table 7.5), roughly the depth range in which the Fe and Mn redox reactions occur. This suggests a possible association between the two, particularly as both the Fe^{3+}-Fe^{2+} and the Mn(IV)-Mn^{2+} couples are known to be electroactive with respect to a platinum electrode (Morris and Stumm, 1967). Table 7.5 shows pE values calculated for various redox reactions. Doyle (1968) observed that the redox potential of interstitial waters often corresponds to that calculated for the τ-FeOOH-Fe^{2+} couple. Although pE values calculated using this couple are reasonably close to those observed, the problem remains of not being able to truly recognize the reaction which controls pE as measured by a platinum electrode. This probably reflects the fact that observed pE values are rarely due to any one redox reaction and that true thermodynamic equilibrium does not exist in natural waters as a result of slow reaction kinetics (Morris and Stumm, 1967).

Finally it should be noted that although Mn and Fe redox reactions also involve protons, the deep waters at Mo 49, Bo 1 and Bo 3 are sufficiently well buffered to prevent any significant change

TABLE 7.5

Calculated pE values for various reactions at Bo 1

Depth (m)	Observed pH	$-\log a_{Fe^{2+}}$	$-\log a_{Mn^{2+}}$	Observed pE	A	B	C
40	6.62	7.39	8.04	+5.78	+11.20	+6.80	+3.89
50	6.65	7.79	6.14	+5.42	+10.19	+7.11	+4.20
55	6.66	6.82	5.39	+1.78	+9.79	+6.11	+3.20
60	6.66	5.79	5.39	+0.33	+9.79	+5.08	+2.17
65	6.61	5.84	5.43	-1.22			

A pE calculated from $\frac{1}{2}\ MnO_2(s) + 2H^+ + e = \frac{1}{2}\ Mn^{2+} + H_2O$ $pE^o = 20.42$
(Stumm and Morgan, 1970)

B pE calculated from $Fe(OH)_3 + 3H^+ + e = Fe^{2+} + 3H_2O$ $pE^o = 19.27$
(Krauskopf, 1967)

C pE calculated from γ-$FeOOH + 3H^+ + e = Fe^{2+} + 2H_2O$ $pE^o = 16.36$
(Doyle, 1968)

$-\log a_{Fe^{2+}}$ = negative logarithm of Fe^{2+} activity assuming an activity coefficient of 0.3

$-\log a_{Mn^{2+}}$ = negative logarithm of Mn^{2+} activity assuming an activity coefficient of 0.3

of pH with depth even across the O_2-H_2S boundary (Table 7.5).

7.6 Discussion of the Nature of the Authigenic Iron and Manganese Phases

The Mn(IV) solid phase in the particulate matter (see a, Fig. 5.1) and in the surface layer of some sediments from Osterfjord in all probability occurs as a hydrous oxide. It is brown in colour and appears to be amorphous to X-rays as are particulate manganese oxides in lake waters (Delfino and Lee, 1968). The initial products of Mn(II) oxidation cannot be characterised in terms of a simple stoichiometry and may display a degree of oxidation from $MnO_{1.3}$ to $MnO_{1.9}$ under slightly alkaline conditions (Stumm and Morgan, 1970). Anomalously high concentrations of some particulate major elements relative to Si, Al and Ti (assumed to be diagnostic of silicate material) coincide with the highest particulate Mn contents at Mo 49 and to a lesser extent at Bo 2 (p. 39). Levels of these elements are often far in excess of the concentrations that could be expected in sea salt on the filter papers as measured by Cl analysis. The relative order of enrichment is $Ca > S > P \gg K + Mg$. S and P are probably associated with exceptionally high particulate organic matter contents (p. 42). Although Ca may be present as inorganic, perhaps even authigenic calcite in the deep waters of Hofjord (see c in Fig. 5.1), the association between Ca, Mg, K and Mn is possibly a result of adsorption on to the Mn(IV) phase. Ca^{2+} is known to be adsorbed preferentially to Mg^{2+} and K^{+} by colloidal hydrous MnO_2 (Posselt et al., 1968) possibly explaining why it is enriched in the particulate matter relative to K and Mg. Under experimental conditions (pH = 5, ionic strength = 1×10^{-2}) Posselt et al. (1968)

found that 0.113 mole Ca/mole MnO_2 was adsorbed compared to 0.10 mole Ca/mole Mn at 210m in the profile at Mo 49 (assuming all non-silicate Ca is adsorbed by Mn(IV) phase).

The Fe(III) solid phase also appears to be X-ray amorphous. Stumm and Morgan (1970) suggest that it is most likely to be poorly crystallized FeOOH although it is usually termed 'hydrous ferric oxide' ($Fe_2O_3 . nH_2O$) or 'ferric hydroxide' ($Fe(OH)_3$). There is a good association between the distributions of excess particulate Fe(III) and total particulate P at Bo 1 and Bo 3 (Figs. 7.3 and 7.5) and to some extent at Mo 49 and Bo 2 (Figs. 7.2 and 7.4). Values quoted for the ZPC[2] of '$Fe(OH)_3$' or its equivalent show a range of pH values from about 6 to 8.5 (Stumm and Morgan, 1970). Therefore the surface charge on the Fe(III) solid phase may be positive or negative at pH values observed in the fjords (p. 30). Ions that form insoluble compounds or undissociated complexes with a component of a solid phase are adsorbed relatively strongly irrespective of electrostatic attraction (Parks, 1967). As Fe(III) and P form both (e.g. strengite, $FePO_4 . 2H_2O$ (Nriagu, 1972) and $FeH_2PO_4^{2+}$, $FeHPO_4^{+}$ (Stumm and Morgan, 1970)), it is reasonable that a close affinity should exist between them. However it is doubtful whether surface adsorption alone could account for the very high molar P/Fe ratios observed in the solid phase (average = 0.66, calculated on an organic free basis) although insufficient P exists for the phase to

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2 ZPC = zero point of charge.

be strengite. According to Stumm and Morgan (1970) a mixed ferric hydroxo-phosphate is likely to be precipitated with its OH^-/PO_4^{3-} ratio related to the pH of the system. A similar Fe-P phase has been observed in surface and intermediate waters of Loch Etive (Price and Calvert, 1973).

The Fe(II) solid phase[3] is black in colour and unstable under atmospheric conditions. In the presence of the observed sulphide concentrations within the inner basin of Bolstadfjord (maximum of 200 µg ats/l at Bo 4) Fe(II) sulphide is the most stable phase (Berner, 1971). Generally it is termed hydrotroilite (e.g. Ostroumov et al., 1961; Volkov, 1961a; 1961b; Kaplan et al., 1963) but Berner (op. cit.) suggests that it is really a mixture of metastable sulphides such as mackinawite (tetragonal $Fe_{1+x}S$) and greigite (cubic Fe_3S_4). Unfortunately it is not possible to obtain an estimate of the Fe/S molar ratio of the phase due to the presence of elemental sulphur in particulate matter samples from anoxic waters (p. 41).

3 That occurring in the water column of the inner basin of Bolstadfjord (Bo 1 and Bo 3) and in some at least of the anoxic sediments (in addition to pyrite).

CHAPTER 8

SUMMARY AND CONCLUSIONS

The hydrography and hydrochemistry of a group of fjords to the north of Bergen have been studied in an attempt to understand the distribution of suspended particulate matter and chemical transformations involving Fe, Mn and related elements in the waters. In addition the chemical composition of the sediments has been investigated to see how their terrigenous and authigenic components relate to the chemistry of the overlying waters and suspended particulate matter.

The main hydrographic and hydrochemical features of the surface waters are similar in all the fjords. There is invariably a low salinity, outflowing, surface water layer which is underlain by a marked halocline and coincident pycnocline. The low salinity layer is most evident in Bolstadfjord while it exhibits a decreasing development in Mofjord, Molviksfjord and Osterfjord. Within the fjords it seems that a more or less normal estuarine circulation pattern exists at least for the near-surface waters. However there are considerable differences between the deep water characteristics of the fjords, the most significant being in the relative position of the O_2-H_2S boundary. In Osterfjord the boundary occurs within the surface (~2cm) sediments while the overlying waters are fairly well ventilated throughout. In Mofjord, Molviksfjord and the middle basin of Bolstadfjord the boundary occurs at or very close to the

sediment-water interface whereas in the inner basin of Bolstadfjord it occurs in the water column some 30m above the sediments. The deep waters of Hofjord and Molviksfjord appear to be fairly isolated from the surface waters although internally well-mixed. On the other hand both the inner and middle basins of Bolstadfjord generally contain very poorly mixed deep waters. The hydrographic conditions in the different fjords are clearly related in some way to sill depth. For example the relatively low density of the bottom waters in Bolstadfjord (σ_t = 17.3) is the same as that at sill depth outside the fjord giving credence to the idea that bottom waters are renewed by advection over the sill. Examination of the data however shows that it is not possible to characterize the development of anoxic conditions using any one factor such as sill depth or amount of runoff.

Anoxic conditions in the deeper waters of the inner basin of Bolstadfjord are associated with a build up of dissolved phosphate-P, silicate-Si and titration alkalinity far in excess of their normal sea water concentrations. This feature, together with the decrease in dissolved O_2 with depth at every water station, has been attributed to the decomposition of organic matter and to the partial dissolution of diatomaceous material in either the waters, the sediments or both. In general however the observed concentrations of decomposition products do not coincide with those predicted using the stoichiometric model of Redfield et al. (1963).

The observed distribution of suspended particulate matter is probably characteristic of fjords in general where a surface estuarine

circulation is strongly developed. It is related to three factors:-

a) Circulation: a maximum of detrital particulate matter often coincides with the pycnocline largely because the latter acts as a barrier to settling. A considerable amount of the fine-grained, river borne detritus may escape the fjord via its surface outflow despite the presence of shallow sills. Most of the detrital material penetrating the pycnocline probably then sinks relatively rapidly through the deeper waters. Surface waters (those above the pycnocline) as a whole usually have higher detrital particulate matter contents than do intermediate waters, whereas deep waters are more variable in this respect and also in the composition of their detrital constituents. In Osterfjord a high concentration of particulate matter in the bottom waters is due to resuspension of underlying sediments whereas in the more restricted bottom waters of the other fjords there is no such resuspension.

b) In situ biological production: the highest concentrations of biogenic matter, produced in situ, seem to occur in the surface waters but do not always coincide with the pycnocline.

c) Physico-chemical processes: river borne colloidal Fe(III) may be precipitated as '$Fe(OH)_3$' by the saline fjord waters. In sub-surface fjord waters the distributions of Mn, Fe and related elements are affected by redox reactions and diffusion-advection processes.

Over half the suspended particulate matter always comprises biogenous material including planktonic skeletal matter which is mainly diatoms. The surface waters predominantly contain either fresh water or marine diatoms apparently depending on the thickness and salinity of the outflowing water layer. The major inorganic components of the particulate matter are well-crystallised 10Å micaceous material and to a varying degree quartz and solid phases of Fe and Mn. While particulate K, Mg, Al and Ti are predominantly associated with detrital silicates, particulate Si and Ca are additionally held in diatoms and skeletal carbonates respectively. Particulate P and S probably exist, at least in the surface waters, largely as biogenic matter.

The nature of the suspended particulate matter is in several respects quite unlike that of the underlying sediments. The particulate matter appears to be enriched in micaceous material relative to quartz and feldspar. This has been attributed to the preferential settling of quartz and feldspar grains through the water column and is reflected in the chemical composition of the sediments and particulate matter (as indicated by element/Al ratios). The latter ratios may in addition be affected through the adsorption of K^+ and Mg^{2+} by clay minerals. Biogenous material constitutes a much larger fraction of the total particulate matter than of the sediments due to the presence of a biomass in the fjord waters and to recycling of organic matter as a result of its decomposition.

The distributions of Fe and Mn can be discussed both with respect to their association with aluminium-silicates and their

participation in redox reactions. Particulate Fe and Mn are associated mainly with detrital ferromagnesian minerals in the river and surface fjord waters as well as in most of the underlying sediments. However the distributions of dissolved and particulate Mn are also related to the position of the Mn(IV)-Mn(II) redox boundary ($\sim O_2$-H_2S boundary) irrespective of whether it coincides with the sediment-water interface or occurs within the water column. The same is true for Fe where the Fe(III)-Fe(II) redox boundary ($\sim O_2$-H_2S boundary) occurs in the water column although it has not been confirmed at the sediment-water interface. Where the O_2-H_2S boundary exists in the water column relatively large dissolved and small suspended particulate matter concentrations of these two metals occur below the boundary as opposed to low dissolved and high particulate concentrations above. These features have been interpreted by using vertical diffusion and pE models. It is supposed that Mn(IV) and Fe(III) oxides-hydroxides settle through the water column until reduced to Mn(II) and Fe(II) at the appropriate redox boundary and hence solubilised. Consequently a reservoir of dissolved Fe(II) and Mn(II) is established beneath the redox boundaries. Upward flux of part of this Fe(II) and Mn(II) (through vertical diffusion) and subsequent oxidation above the relevant redox boundary causes the reprecipitation of Fe(III) and Mn(IV) phases. This process will maintain the observed profiles as long as Fe and Mn are continually supplied from surface waters. A similar mechanism is envisaged to produce the Mn profile where the O_2-H_2S boundary coincides with the sediment surface, although in this instance upward

flux of Mn(II) below the boundary (i.e. within the surface sediments) may occur due to sediment compaction. Unless removed by physical processes the concentrations of the divalent species below the O_2-H_2S interface will continue to increase until precipitation occurs. The solubility of Fe(II) is sufficiently low that Fe sulphides can precipitate in every instance. However only in the middle and outer basins of Bolstadfjord does an analogous situation exist for Mn, where it has been shown that a mixed Mn-Ca carbonate is precipitated in the sediments.

The sediments, which are all probably post-glacial in age, have been divided into oxic and anoxic from evidence concerning their composition and situation relative to the O_2-H_2S boundary. The oxic sediments are exclusive to Osterfjord and mainly comprise blue-grey and green-grey homogeneous silts and clays. Some have a reddish-brown surface layer due to the presence of Fe(III) and Mn(IV) oxides-hydroxides. In contrast most of the sediments sampled in Mofjord, Molviksfjord and Bolstadfjord are strongly anoxic and comprise organic-rich, irregularly laminated clays and silts. Certain organic-poor horizons in Bolstadfjord and shelly horizons (mainly bivalves) elsewhere appear to have originated largely as a result of slumping.

The mineralogy and chemical composition (indicated by oxide/Al_2O_3 ratios) of the lithogenous fraction of the sediments suggest that Fennoscandian glacial and post-glacial clays are their major source. In addition, Si occurs as diatoms; Ca, CO_2 and Sr as calcareous skeletal material, largely bivalves; and P is held in

organic matter. The only elements whose contents consistently differ between oxic and anoxic sediments are organic C, S and Mo; they are all enriched in the anoxic sediments except for the slumped horizons in Bolstadfjord. S enrichment has been attributed to the presence of authigenic sulphides including pyrite. That of organic C has a more complex origin but is probably related to a higher relative rate of organic matter deposition in Bolstadfjord, Mofjord and Molviksfjord and possibly to its less efficient decomposition under anoxic conditions. In the first instance at least Mo seems to be incorporated into the anoxic sediments via co-precipitation with Fe sulphides.

There are marked surface enrichments of Zn, Pb and sometimes of Cu in all but one sediment core (oxic and anoxic). Exceptionally no surface metal enrichment occurs in sediments sampled near to the mouth of the River Moelv. Two alternative explanations are given for this metal enrichment; they are heavy metal pollution and/or a natural recycling process involving the release of bound metals during organic matter decomposition in the surface sediments. The latter is favoured since there is no evidence of any pollution in the area. However it is considered likely that elsewhere pollution may exaggerate this otherwise natural phenomenon.

APPENDIX A

General Shipboard Procedure, Sample Collection and Preparation

i) General shipboard procedure

The procedure given below was generally followed at each station although one or more of the steps may have been omitted at any station:-

a) Determination of geographical position and water depth (p. 94).

b) Determination of salinity and temperature profiles (p. 100).

c) Determination of dissolved oxygen profile (if 'oxygenmeter' was being used; p. 101).

d) Water sampling (p. 95).

e) Coring (p. 97).

ii) Determination of geographical position and water depth

There was no need for a very accurate determination of geographical position since sampling strategy was to occupy one or two stations in the central part of each basin in order to determine its general geochemical character. Consequently, it was sufficient to ascertain visually the location of each station. Due to the narrowness of the fjords, it is estimated that the positions determined in this way are accurate to within $\pm$200m except in Osterfjord where the accuracy is probably nearer $\pm$500m.

An initial determination of water depth at each station was obtained with a SIMRAD echo-sounder (depths of water sampling and

coring were measured by 'metre-wheel'.

iii) Water sampling

An array of four 7.5 l N.I.O.[1] polyvinyl chloride/nylon water bottles was used to sample water. Immediately on retrieval of a bottle, a number of sub-samples were collected. For this purpose, a plastic-tubing extension was fitted over the bottom tap of the N.I.O. bottle in order to minimise bubbling. During the 1971 cruise nitrogen gas was used to flush out the N.I.O. bottles when sulphide-rich waters were collected, but apparently this did not prevent oxidation of the sample (see p.116). Sub-sampling, completed within ten minutes of sample recovery, was as follows (not all sub-samples were collected in every instance):-

a) an 'oxygen bottle' (one with a ground glass, tapered stopper) was filled almost until overflowing. The sub-sample was immediately treated with 1ml $MnCl_2$ solution and excess (1ml) of a KOH/KI solution after which the bottle was stoppered, care being taken to exclude all air, and shaken. The sub-sample was kept cool and in the dark until its dissolved oxygen content was determined (Winkler method; p. 101), not more than two weeks later.

b) the same type of air-tight bottle was used to collect a sub-sample for dissolved H_2S measurement (p. 101). Again care was taken to exclude all air from the bottle which was stored for no more than 3 hours in a cool, dark place prior to analysis.

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1 National Institute of Oceanography, now Institute of Oceanographic Sciences.

c) a glass vessel, specially adapted for pH, Eh and pS^{2-} analysis (p. 102), was filled to overflowing directly from the N.I.O. bottle. Their measurement was completed within 10-15 minutes of sample recovery.

d) a 250ml reagent bottle was filled and stored in a cool, dark place for the determination of titration alkalinity (p. 104), no more than 24 hours later.

e) a sub-sample for nutrient analysis (dissolved phosphate and silicate; see p. 104) was collected in a separate 250ml reagent bottle. Following storage in a cool, dark place, the analysis was commenced within 5 hours of sampling.

f) the remainder of each sample was collected in an acid-washed polyethylene jerry can following a single rinse with about 250ml of the water sample. This sub-sample was then stored until filtration which was commenced within 6 hours. Filtration was carried out during all three cruises using a SARTORIUS vacuum filtration system and SARTORIUS membrane filters (composed of cellulose nitrate, pore size = 0.45μ, diameter = 47mm). In an attempt to remove any retained sea salt, the filter papers were washed several times with ~20ml doses of membrane filtered (0.45μ), deionised/distilled water (M.D.D. water). However after the detection of a halite peak in some diffractograms of 1970 suspended particulate matter samples, it became apparent that this washing method was not altogether successful and that a correction factor would have to be applied to the analytical results of certain elements (see p. 116). After being washed, the filter papers were stored in dry, acid-washed, M.D.D. water-rinsed petri-dishes in which they were kept

until analysed. The filtrate was run back into a jerry can and weighed in order to determine the amount of water filtered. Finally, the pH of the filtrate was lowered to about 2 with 6N ARISTAR HCl.

A drawback of the SARTORIUS filtration system is that it is open to the atmosphere, and it was thought that this may have been the cause of the apparent sulphide oxidation (p. 41). In 1972 therefore, a closed filtration system was used as well. This uses a nitrogen gas pressure of 12psi to force sea water through a NUCLEPORE membrane filter (composed of a high molecular weight polycarbonate, pore size = 0.4μ, diameter = 37mm) and is similar to the method employed by Spencer et al. (1972). Unfortunately filtration by this method did not prevent the occurrence of anomalously high S concentrations in samples from anoxic waters, but it was found that by using NUCLEPORE filter papers it is possible to remove residual sea salt almost totally by washing.

iv) Coring

A stainless steel, gravity corer with plastic core liner (6cm diameter) was used to sample sediments. In most cases a single core was collected at each station for sediment analysis, but at some stations an additional core was obtained for interstitial water sampling.

a) cores for sediment analysis: immediately on retrieval of the coring device, the plastic liner (transparent) was removed and the core length (cm), presence or absence of H_2S (smell), and general lithology of the sediment core were noted. The plastic liner was sealed at both ends with plastic caps, and most of the water overlying

the sediment was drained off by boring a hole through the liner about 4cm above the sediment surface. The core liner was then resealed with P.V.C. tape and stored upright until the sediment was frozen (in dry ice), some hours later. On their return to Edinburgh, the frozen cores were cut longitudinally into half with a CLIPPER masonry saw. The newly exposed surface of each half was rinsed clean with tap water. One half of the core was used to obtain a more detailed lithological description of the sediment (Appendix E) and was then removed to a cold store (4°C), resealed in plastic drain-piping, for storage as archive material. The other half was sub-sampled. The cores from all the fjords except Bolstadfjord were divided into equal units of either 2, 5 or 10cm as their lithology was constant throughout. The sediment cores from Bolstadfjord were divided according to lithological units (p. 46). Each sub-sample was dried at 110°C and then ground (homogenised) to a fine powder (200 mesh) using a tungsten carbide TEMA disc mill.

b) cores for interstitial water sampling: sediment cores for interstitial water extraction were initially stored upright and un-frozen. Each core was divided either into 10cm units or into lith-ological units (in the case of Bolstadfjord sediments) as the sedi-ment was extruded from the plastic core liner with a plunger. The sediment units were immediately transferred to nylon squeezers, similar to that described by Reeburgh (1967). The pore waters were expressed at a pressure (nitrogen) of 60–100psi, collected in acid-cleaned 250ml polythene bottles, filtered through 0.45μ SARTORIUS membrane filters (using the same system as that described above),

and finally taken to pH 2 with 6N ARISTAR HCl. The interstitial water samples were immediately frozen and, together with the 'squeezed' sediments, transported to Edinburgh. Pore water extraction was completed within about 12 hours of coring at a temperature which was close to that in situ (~5°C).

On thawing the interstitial water samples in Edinburgh, it became apparent that a brown precipitate existed in most of them. The samples were therefore filtered in an identical fashion to that used after 'squeezing' (p. 98), and the precipitate qualitatively analysed by X-ray fluorescence. Of the metals to be determined, only Fe was detected. Bray et al. (1973) observed the oxidation of Fe(II)(aq.) to Fe(III)(s) during sampling of anoxic interstitial waters. In the present study however, it is evident that precipitation must have occurred sometime after 'squeezing' as the pore water was filtered following this step. Preliminary infrared absorption spectrometry studies (M. Krom, pers. comm.) suggest that the precipitate is composed largely of humic material (acid insoluble). Thus acidification of the samples may have caused the precipitate to form.

APPENDIX B

Shipboard Analytical Methods

This section includes details of all analytical methods which had to be completed within a short time period after sampling. Some of these analyses were undertaken in a land-based laboratory due to lack of space and facilities aboard ship.

i) Salinity and temperature

Salinity and temperature were measured in situ with a N.I.O. portable Salinity-Temperature Bridge (Type N.C.5). Readings were possible to a maximum depth of 120m due to the limited length of cable that can be used with the type of instrument.

Salinity and temperature readings were calibrated daily at sea against Standard Copenhagen Sea Water ($S‰ = 35.00$) and a laboratory, Hg thermometer respectively. Prior to each set of measurements, the electrodes were cleaned with mild detergent and a test-tube brush. Readings were taken as the probe was lowered through the water column, and depth was determined by means of metre markings on the cable itself which was kept as near to the vertical as possible. The estimated precision for temperature determinations is $\pm 0.2^{\circ}C$, estimated accuracy $\pm 1.0^{\circ}C$. During the 1970 cruise, temperature readings were erratic so that these values may be exceeded. Estimated precision for salinity is $\pm 0.1‰$, estimated accuracy $\pm 0.5‰$.

ii) Dissolved oxygen

Dissolved O_2 was measured by an electrode potential method in 1970 and 1972, and by the Winkler (1888) Method in 1971. It was intended to calibrate the two methods and to use them to complement each other, but unfortunately they were never simultaneously operative.

a) potentiometric method: dissolved O_2 saturation relative to that in the surface water was measured in situ with an 'oxygenmeter' and Mackereth electrode (Mackereth, 1964) manufactured by QUALITY MONITORING INSTRUMENTS, London. The system is slightly sensitive to temperature variation and turbulence but because the observed changes in dissolved O_2 were large these factors could be ignored. Readings were taken as the electrode was lowered through the water column and depth was again determined by means of metre markings on the cable. While readings were being taken, the probe was gently moved up and down to ensure a constant flow of sea water over the electrode. The latter was kept in clean sea water when not in use.

b) Winkler Method: the Winkler titrations were carried out at the Geophysical Institute (Avd. A) of Bergen University by Jan Aure.

iii) Dissolved hydrogen sulphide

Dissolved H_2S was determined by an electrode potential method in 1971 and by a colourimetric method in 1972.

a) potentiometric method: a silver-silver sulphide electrode was prepared from an ACTIVION silver billet electrode and calibrated according to Berner (1963) using a saturated calomel electrode as reference. The electrode potential was measured with an ORION specific ion meter (model 407). Calibration of the silver-silver

sulphide electrode was undertaken both before (in Edinburgh) and after (at the Chemistry Institute, Bergen University and back in Edinburgh) the 1971 cruise (Fig. B.1). The calibration line, obtained by combining all the points, was used to relate electrode potential ($E_{S^=}$) to pS^{2-} by the following equation (assuming $10^{-21.9}$ is the equilibrium constant for $H_2S(g) = 2H^+(aq.) + S^{2-}(aq.)$):-

$$pS^{2-} = 21.9 - 2pH$$

A description of the analytical procedure is given below.

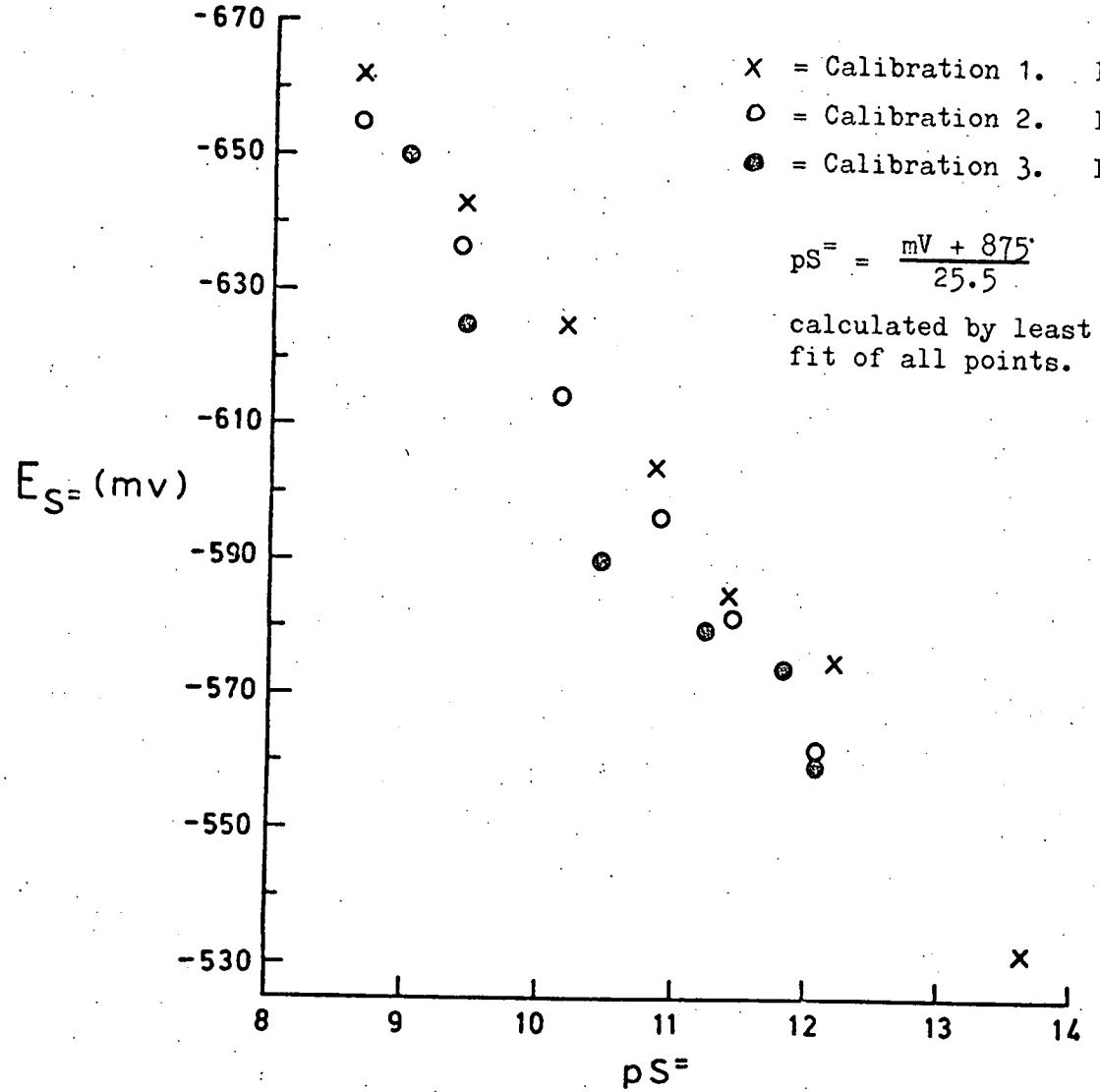
b) colourimetric method: dissolved H_2S was determined colourimetrically in the land-based laboratory employing the method described by Cline (1969). A single mixed diamine reagent is used comprising N,N-dimethyl-p-phenylenediamine sulphate and ferric chloride dissolved in HCl. The author gives a value of $\pm 2\%$ for both precision and accuracy.

iv) <u>pH and Eh</u> (and pS^{2-})

The pH, Eh and pS^{2-} of each water sample were monitored simultaneously aboard ship within minutes of sampling. The glass flask, used to collect sub-samples for this purpose (p. 96), was adapted to take four electrodes and a Hg thermometer which were all fitted with ground-glass collars so that an air-tight seal could be maintained. An ACTIVION combination glass electrode was used to measure pH and an ORION combination platinum electrode to measure Eh (the other two electrodes fitted into the flask were the sulphide electrode and the calomel (reference) electrode). Electrode potentials were measured using an ORION specific ion meter (Model 407). Temperature was monitored to the nearest $0.1^{\circ}C$ while readings were being taken.

Fig. B.1

Calibration graph for the silver-silver sulphide electrode



	$E_{S^=}$ (mV)	pH	$pS^=$
Calibration 1	-532	4.14	13.62
	-572	4.85	12.20
	-604	5.52	10.86
	-625	5.87	10.16
	-643	6.25	9.40
	-662	6.62	8.66
	-680	6.96	7.98
Calibration 2	-562	4.91	12.08
	-582	5.27	11.44
	-597	5.51	10.88
	-615	5.89	10.12
	-637	6.27	9.36
	-655	6.63	8.64
Calibration 3	-560	4.92	12.06
	-574	5.04	11.82
	-580	5.32	11.26
	-590	5.72	10.46
	-625	6.24	9.42
	-650	6.46	8.98

Prior to examination of each sub-sample, the glass electrode was calibrated against TRIS buffers of pH 7.4 and 8.0 (Smith and Hood, 1964) and the platinum electrode against Zobell solution (Zobell, 1946). The electrodes and Hg thermometer were then inserted into the overflowing glass vessel, which also contained a Teflon-coated, magnetic stirring rod, thus excluding all air. Finally the electrode potentials and temperature were measured while the sub-sample was being stirred. In between measurements, the glass electrode was cleaned in distilled water and the platinum electrode with laboratory tissue. All electrodes were stored in clean sea water when not in use.

pH measurements were corrected for the temperature change from in situ to laboratory conditions ($dpH/dt = -0.011 pH/1^{\circ}C$ rise); the pressure effect ($dpH/dp = +0.232 pH/1000$ bars rise) is negligible at all fjord depths (see Li et al., 1969). Eh was corrected for temperature effect and calomel half cell potential according to Zobell (1946).

v) Dissolved phosphate and silicate

The terms 'dissolved phosphate' and 'dissolved silicate' as used in this thesis need to be defined. There are several ways of categorising phosphorus in natural waters (Stumm and Morgan, 1970). Here 'dissolved phosphate' is, more correctly, that part of the total phosphorus content which will react with acidified molybdate solution within 5 minutes or in other words 'reactive phosphorus' (after Strickland and Parsons, 1968). The major constituent of this fraction is the orthophosphate ion although an unknown, relatively small amount

or organic, soluble phosphorus and that fraction of the element associated with Fe(III) solid phases (p. 85) will also contribute. Similarly 'dissolved silicate' is a working definition and includes all forms of silica that will react to form a silico-molybdate complex ('reactive silicate'). Although not encompassing all forms of dissolved silica, it probably gives a reasonable measure of the amount readily available for biological and chemical reactions (Strickland and Parsons, op. cit.).

Phosphate and silicate were determined in unfiltered water samples exactly as described by Strickland and Parsons (op. cit.) for 'reactive' phosphorus and silicate except that anoxic water samples were purged of their H_2S content prior to analysis by flushing with nitrogen gas for about 1 hour. The latter was to prevent any possible interference by H_2S on complex formation. Estimated precision for the phosphate method is ± 0.03 µg at./l, and for the silicate method is ± 2.5 µg at./l.

A UNICAM SP600 (series 2) spectrophotometer was used for all colourimetric determinations.

vi) Titration alkalinity

Titration alkalinity was determined in the shore laboratory using the potentiometric method of Edmond (1970) which involves titrating the sub-sample with HCl in a closed system. An ACTIVION combination glass electrode and a PHILIPS digital pH meter (PW 9408) were used to measure pH. 0.5 or 1.0N volumetric grade HCl was introduced into the specially adapted analytical vessel (see Edmond, 1970) with a GILMONT micrometer screw burette (2ml capacity) and was accommodated in the system by displacement of part of a 5ml SEGMA

glass hypodermic syringe. The titration data was processed using a program written by I. Davies and based on that described by Edmond (op. cit.). The estimated accuracy of the method is ±2%.

APPENDIX C

Laboratory Analytical Methods

This section includes all analytical methods undertaken at the Grant Institute of Geology in Edinburgh.

i) Dissolved transition metals (Fe, Mn, Cu, Zn and Ni) in fjord and river waters

The method (solvent extraction/Atomic Absorption Spectrometry (A.A.S.)) used to determine the concentrations of dissolved Fe, Mn, Cu, Zn and Ni in fjord and river waters is similar to that of Duchart et al. (1973) for trace metals in interstitial waters. However, the standardisation and extraction procedures differ sufficiently as to require a brief summary.

4 x 400ml portions of each sample were transferred into 500ml separating funnels. Double quantities were used for blanks (double distilled, deionised water). A dose of 0, 1, 2 and 4ml of a mixed metal standard solution was pipetted into the four portions of each sample. 10ml of 6% w/v NaK tartrate was added to each funnel (to keep Fe and Mn in solution at higher pH) and after 10 minutes the pH was raised to just over 6 with 2N A.A.S. grade Ammonia. 5ml of 10% w/v Analar sodium diethyl dithiocarbamate (NaDEDTC) was then added to each funnel followed by 20ml of A.A.S. grade 4-Methylpentan-2-one (MIBK) after a further 10 minutes. The funnels were then shaken for 30 minutes and allowed to rest for 20 minutes. The bottom, aqueous layer was discarded while the organic layer was run into

stoppered silica test-tubes.

The metal contents of the organic solutions were determined with a VARIAN-TECHTRON AA4/AA5 atomic absorption spectrophotometer. Non-atomic absorption was corrected for using a TECHTRON Hydrogen Lamp. The analytical precision[1] for the various elements, based on 6 replicates, is given in Table C.1. The reason why the values are so high, especially for Ni and Cu, compared to the values for interstitial water analysis is that the concentrations were very low and in some cases were almost at the limits of detection.

ii) Dissolved transition metals in interstitial waters

The method of analysis for transition metals in interstitial waters is the same as that described above except for the volume of sample (50 or 25ml) and reagents used (2ml of tartrate, 2ml of NaDEDTC, 20ml of MIBK). In addition it was not possible to employ a standard addition method because of the small volume of sample available (maximum ~100ml), so a set of standards was prepared by spiking double distilled, deionised water with the original mixed standard. It was found that the variation in MIBK solubility between saline fjord water and distilled water is insignificant when such small initial volumes of sample and standard are used. There was also very little difference in non-atomic absorption between standards and samples. The analytical precision based on 6 replicates is shown in Table C.1.

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1 Unless otherwise stated precision is expressed as the coefficient of variation (V_x):

$$V_x = \frac{\sigma_x}{\bar{x}} \cdot 100\%$$

where σ_x = sample standard deviation and $\bar{x}$ = sample mean.

TABLE C.1

Analytical precision for dissolved transition metal analysis

	Fjord/river waters	Interstitial waters
Mn	±5%	±3%
Fe	±12%	±2%
Zn	±11%	±8%
Ni	±100%	±24%
Cu	±100%	±6%

iii) Sediment mineralogy

The dried, ground (200 mesh) sediment powders (p. 98) of cores Bo 1 and Bo 6 were prepared for X-ray diffraction by being pressed into aluminium holders, with a coarse grade WHATMAN filter paper placed between the holder and the press. The purpose of the filter paper was to ensure that a randomly orientated sample was obtained. A PHILIPS X-ray diffractometer (PW 1011/1050) was employed with Ni filtered Cu radiation (Cu Kα). Each sample was scanned once from a high (40° 2θ) to a low angle (4° 2θ). The halite reflection (2.82Å) was used as an index peak because it was present on every diffractogram and was sharp. The criteria used for identification are indicated briefly on p. 47 .

iv) Major elements in sediments

Most major elements (Ca, K, Fe, Ti, Al, Si, Mg, P and Mn) were determined by X-ray fluorescence spectrometry employing an analytical method similar to that described by Rose et al. (1963). With the exception of Mn, which was analysed on a PHILIPS PW 1540 single-channel spectrometer, all the elements were determined using a PHILIPS PW 1212 multi-channel spectrometer.

A mixture of dried, powdered (200 mesh) sediment, lanthanum oxide (heavy absorber) and lithium tetraborate (flux and dilutent) in the ratio 1:1:8 was fused at 1050°C for 20 minutes. When cool, the fused beads were made up to their original weight by further addition of $Li_2B_4O_7$, thus compensating for the loss of volatiles. The samples were then reground in a TEMA tungsten carbide disc mill for 2 minutes and redried at 110°C overnight. Finally the samples

were pelletised at 15 tons pressure for one minute with boric acid as backing material. Standards[2] were prepared in an identical manner. The standards and samples were analysed in sets of four, one of which was an internal standard so that machine drift could be monitored and corrected. Instrument conditions for each element are summarised in Table C.2. The output from the PW 1212 spectrometer was in the form of punched tape which was processed (see Appleton, 1970) to give major element concentrations using the facilities of the Edinburgh Regional Computing Centre (ERCC). Output from the PW 1540 spectrometer (Mn analysis) was always processed manually. The analytical (18 replicates of one disc) and overall (6 independently prepared discs) precisions of the method are shown in Table C.3.

v) Sulphur and chlorine in sediments

S and Cl were analysed by X-ray fluorescence spectrometry employing an unfused mixture of sample, La_2O_3, and $Li_2B_4O_7$ (all dried at 110°C) in the ratio 1:1:4. The mixture was homogenised by re-grinding in the TEMA disc mill (1 minute), dried at 110°C and pelletised as described for the major elements. Special standards were prepared by spiking a finely ground (200 mesh) shale with known amounts of NaCl and Na_2SO_4. Instrument conditions are summarised

2 A combination of international and departmental standards was used for all X-ray fluorescence work. In the case of the major elements, the standards are the ones marked with an asterisk in Table C.4 and U.S.G.S. Standards as indicated in Table C.5. Mn is exceptional in that standards 98(a), B3, T-1, and B1 were employed.

TABLE C.2

Instrument conditions for X-ray fluorescence analyses

Element and line		Machine PW-	Tube	kV	mA	Crystal	Peak°	Background(s)*	Method	Counter	EHT (v)	Discrimination L.L.	C.W.	Att.	C.T.	cycles	Coll.	Vac.	S.P.	Notes
Al	Kα	1212	Cr	60	24	PET	144.95	-	Rose	F	1700	A	A	A	40	3	C	Yes	F	
Ca	Kα	1212	Cr	40	8	PET	45.19	-	Rose	F	1700	A	A	A	20	3	F	Yes	F	
Cl	Kα	1540	Cr	50	32	PET	65.36	-	S	F	1775	1.30	3.70	2'	20	5	C	Yes	U	
Cu	Kα	1212	W	80	24	LiF(200)	44.97	44.55, 45.50	Rey	S	1000	A	A	A	40	3	F	No	PD	
Fe	Kα	1212	Cr	60	24	LiF(200)	57.60	-	Rose	F	1700	A	A	A	20	3	F	Yes	F	
K	Kα	1212	Cr	60	24	PET	50.68	-	Rose	F	1700	A	A	A	10	3	C	Yes	F	
Mg	Kα	1212	Cr	40	32	ADP	136.85	133.85	Rose	F	1700	A	A	A	100	3	C	Yes	F	
Mn	Kα	1540	W	60	24	LiF(200)	63.12	-	Rose	F	1700	A	A	A	20	3	F	Yes	F	
Mo	Kα	1212	W	80	24	LiF(110)	28.92	27.92, 29.92	Rey	S	1000	A	A	A	40	2	F	No	PD	
Nb	Kα	1212	W	80	24	LiF(110)	30.44	29.82, 30.92	Rey	S	1000	A	A	A	40	2	F	No	PD	
Ni	Kα	1212	W	80	24	LiF(200)	48.65	48.00	Rey	S	1000	A	A	A	40	3	F	No	PD	
P	Kα	1212	Cr	60	24	PET	89.47	87.47	Rose	F	1700	2.40	3.00	2'	40	3	F	Yes	F	
Pb	Lβ	1212	W	80	24	LiF(200)	28.22	27.92, 28.62	Rey	S	1000	A	A	A	40	3	F	No	PD	
Rb	Kα	1212	W	80	24	LiF(110)	38.00	36.92, 38.52	Rey	S	1000	A	A	A	40	2	F	No	PD	
S	Kα	1540	Cr	50	32	PET	75.63	-	S	F	1775	1.55	2.20	2'	20	5	C	Yes	U	
Si	Kα	1212	Cr	60	24	PET	109.12	-	Rose	F	1700	A	A	A	40	3	C	Yes	F	
Sr	Kα	1212	W	80	24	LiF(110)	35.86	34.92, 36.92	Rey	S	1000	A	A	A	40	2	F	No	PD	
Ti	Kα	1212	Cr	60	24	LiF(200)	86.26	-	Rose	F	1700	A	A	A	10	3	F	Yes	F	
Y	Kα	1212	W	80	24	LiF(110)	33.90	32.92- 34.92	Rey	S	1000	A	A	A	40	2	F	No	PD	Corrected for Rb Kβ
Zn	Kα	1212	W	80	24	LiF(200)	41.76	41.25, 42.25	Rey	S	1000	A	A	A	40	3	F	No	PD	
Zr	Kα	1212	W	80	24	LiF(110)	32.09	30.92, 32.92	Rey	S	1000	A	A	A	40	2	F	No	PD	Corrected for Sr Kβ

* When there were two backgrounds, their counting times were half that for the peak.

Method: Rose = adapted from Rose et al. (1963)
Rey = adapted from Reynolds (1963)
S = special technique using 1:1:4 unfused discs

Counter: F = Flow
S = Scintillation

Discrimination: A = Automatic

Counting time per cycle (C.T.): expressed in seconds

Collimator (Coll.): C = coarse
F = fine

Sample preparation (S.P.): F = fused 1:1:8 mixture
U = unfused 1:1:4 mixture
PD = pressed discs of pure sediment powder

TABLE C.3

Precision of X-ray fluorescence analysis of sediments

Element	Analytical precision	Overall precision of method
Al	±1%	±1%
Ca	±1%	±1%
Cl	±2%	±3%
Cu	±3%	±4%
Fe	±2%	±2%
K	±1%	±2%
Mg	±6%	±7%
Mn	±1%	±5%
Mo	±5%	±5%
Nb	±12%	±12%
Ni	±5%	±5%
P	±8%	±8%
Pb	±6%	±6%
Rb	±5%	±6%
S	±2%	±2%
Si	±1%	±1%
Sr	±3%	±3%
Ti	±2%	±4%
Y	±6%	±6%
Zn	±1%	±1%
Zr	±2%	±3%

TABLE C.4

Standards used for X-ray fluorescence spectrometry

Code	Type of material	Reference
G-2[1]	granite	Flanagan (1969)
GSP-1[1]	granodiorite	ditto
AGV-1[1]	andesite	ditto
DTS-1[1]	dunite	ditto
BCR-1[1]	basalt	ditto
PCC-1[1]	peridotite	ditto
G-1[1]	granite	Fleischer (1969)
W-1[1]	diabase	ditto
98(a)	plastic clay	U.S. National Bureau of Standards
1(a)*	argillaceous limestone	ditto
T-1	tonalite	Thomas (1963)
E1[2]*	ferrogabbro	G.R. Angell (pers. comm.)
E2[2]*	basalt	Clarke (1969)
E3[2]*	fjord sediment	Doff (1970)
520[2]*	basalt	Clarke (op. cit.)
629[2]*	basalt	ditto
630[2]*	basalt	ditto
N 357[2]*	basalt	Jamieson (1969)
QMC I 3[3]*	dolerite	

1 U.S.G.S. Standards
2 Grant Institute of Geology standards
3 Queen Mary College Department of Geology, Geochemistry Laboratories. A Third Report on the Standard Rocks QMC I 1, QMC I 3, QMC M 2, QMC M 3.

* used for major element determinations.

TABLE C.5

U.S.G.S. Standard values
used for X-ray fluorescence spectrometry

	G-2	GSP-1	AGV-1	DTS-1	BCR-1	PCC-1	G-1	W-1
SiO_2	-	67.27	58.99	-	54.48	-	72.64	-
Al_2O_3	-	15.11	17.01	-	13.65	-	14.04	-
Fe_2O_3 (total)	-	4.33	6.80	-	13.50	-	1.94	-
MgO	-	0.95	1.49	-	3.28	-	0.38	-
CaO	-	2.03	4.98	-	6.95	-	1.39	-
K_2O	-	5.48	2.89	-	1.68	-	5.48	-
TiO_2	-	0.69	1.08	-	2.23	-	0.26	-
P_2O_5	-	0.28	0.48	-	0.36	-	0.09	-
MnO	-	0.04	0.09	-	0.17	-	-	-
Cu	10	30	62	5	20	10	-	110
Nb	15	30	20	-	10	3	-	10
Ni	-	13	22	-	18	-	-	78
Pb	31	52	36	12	15	9	-	8
Rb	170	258	70	-	48	-	-	22
Sr	550	250	720	-	340	-	-	190
Y	-	37	24	-	44	-	-	32
Zn	87	100	82	44	115	42	-	82
Zr	330	580	240	-	180	-	-	100

in Table C.2 and the precision (based on sets of 6 replicates) of the method is shown in Table C.3.

vi) Carbonate-C (CO_2) and total-C in sediments

Total-C content was determined by combusting a known weight of dried (110°C), ground (200 mesh) sediment in a LECO[3] induction furnace (model 521-200; fitted with a catalyst furnace (model 507-100) and sulphur and dust traps) and measuring the amount of CO_2 evolved with a LECO carbon analyser (model 572-100). The analytical procedure is fully described in the LECO instruction manual. The accuracy of the instrument was checked at the beginning of each set of readings using LECO steel rings of known carbon content. The overall precision of the method is estimated to be ±3% from 5 replicate analyses.

Carbonate-C was determined using a QUICKFIT reaction flask, condenser and water trap (conc. H_2SO_4) in conjunction with the LECO carbon analyser. Between 0.05 and 3.00g of sediment (depending on expected CO_2 content) was weighed into the reaction flask. 2ml of a 5% w/v ferrous sulphate solution (to prevent hydrolysis of any organic matter) and 2ml of distilled water were added to the flask, which was then fitted to the base of the condenser. A slow stream of oxygen was passed through the sample mixture (to flush out the CO_2) and 3ml of 2N HCl was added. The flask was then warmed gently until boiling when the oxygen flow rate was increased somewhat.

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3 Laboratory Equipment Corporation

When the main receiving flask in the LECO carbon analyser was empty of red liquid, the flow of oxygen was stopped and the burette completely drained of red liquid by turning the valve to 'exhaust'. Finally the amount of CO_2 evolved was measured (see LECO instruction manual). The accuracy of the method was checked at the start of every batch of determinations using a known weight of dried (110°C) reagent grade $CaCO_3$, and the overall precision was determined from 6 replicates to be ±3%.

Organic-C was assumed to be equivalent to the difference between total-C and carbonate-C as measured above.

vii) Trace elements in sediments

Trace elements (Cu, Mo, Nb, Ni, Pb, Rb, Sr, Y, Zn and Zr) in the sediments were measured by X-ray fluorescence spectrometry (invariably the PW 1212) employing the method of Reynolds (1963). 4g of each sediment sample (dried at 110°C, 200 mesh) was pelletised (p. 109). Their mass absorption coefficients (and those of the standards) were then estimated by measuring the intensities of the Compton scattered portion of a $Mo_{K\alpha}$ primary beam (instrument (PW 1540) conditions:- tube at 60kV, 24mA; crystal: LiF(200); peak: 21.13°; counter: scintillation, E.H.T. = 800v, lower level = 2.35, window = 3.55, attenuation = 2'; counting conditions: constant count (10^5) mode used, 5 cycles; no vacuum). The method deviated from that of Reynolds (op. cit.) in that a number of U.S.G.S. Standards were used (see Table C.5) instead of one. Samples and standards were run in a similar way to that described for major element analysis. The spectrometer conditions are summarised in

Table C.2. Straight line calibration curves were constructed by hand and the appropriate parameters inserted into a program, which was used to process the punched-tape output with ERCC facilities. The analytical and overall precision (Table C.3) of the method were determined, respectively, from 6 replicates of the same disc and 6 discs independently prepared from one sample.

viii) Total weight of suspended particulate matter

In 1971 the total weight of suspended particulate matter was determined gravimetrically. Preweighed SARTORIUS membrane filter papers were used for filtration (p. 96). On returning to the laboratory at Edinburgh, the papers were dried in a desiccator and then equilibrated with atmospheric conditions in the balance room in which they had originally been weighed. After a period of about 36 hours the papers were reweighed. No great accuracy or precision is attributed to these results because there was a variable weight loss by the filter papers as a result of the filtration process (see Spencer et al., 1972) and the filters invariably possess a considerable static charge.

ix) Analysis of suspended particulate matter for Ca, K, Fe, Ti, Si, Al, Mg, P, Mn, S and Cl

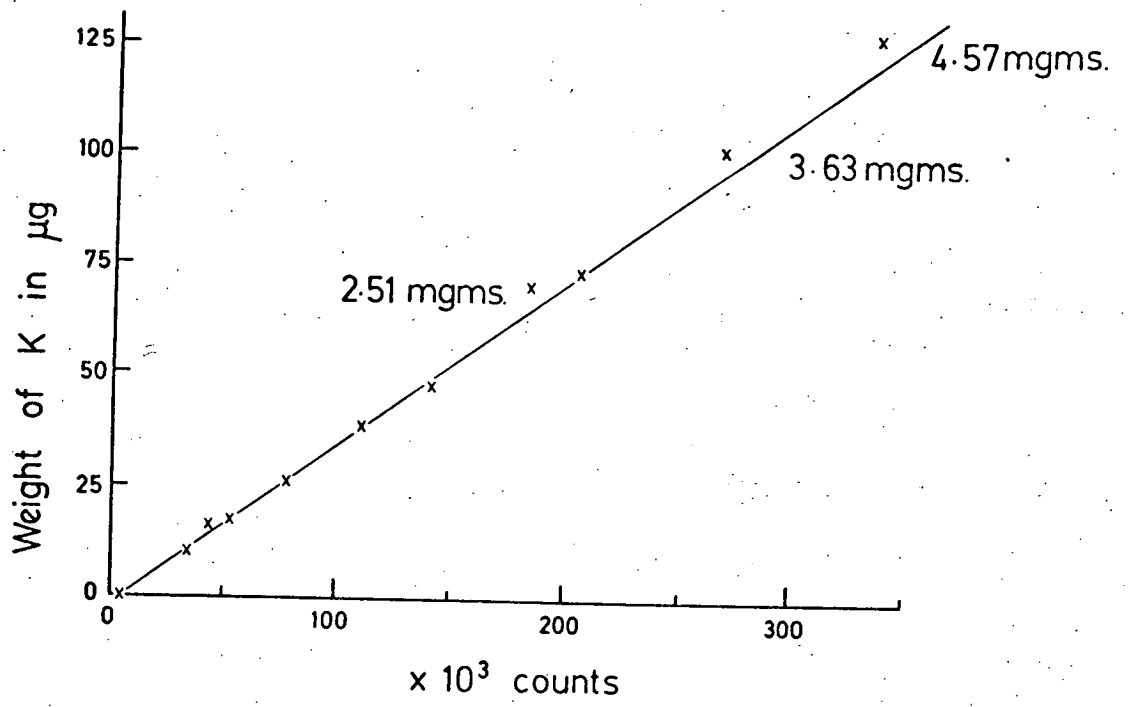
The chemical analysis of suspended particulate matter was undertaken using a thin film X-ray fluorescence technique (PW 1212 spectrometer). Original standards were prepared from 3 contrasting rock types (a basalt, a manganese-rich siltstone, and a greywacké) of known chemical composition. A McCRONE MICRONISING MILL was used to grind the dried (110°C), ground (200 mesh) rock powders even finer,

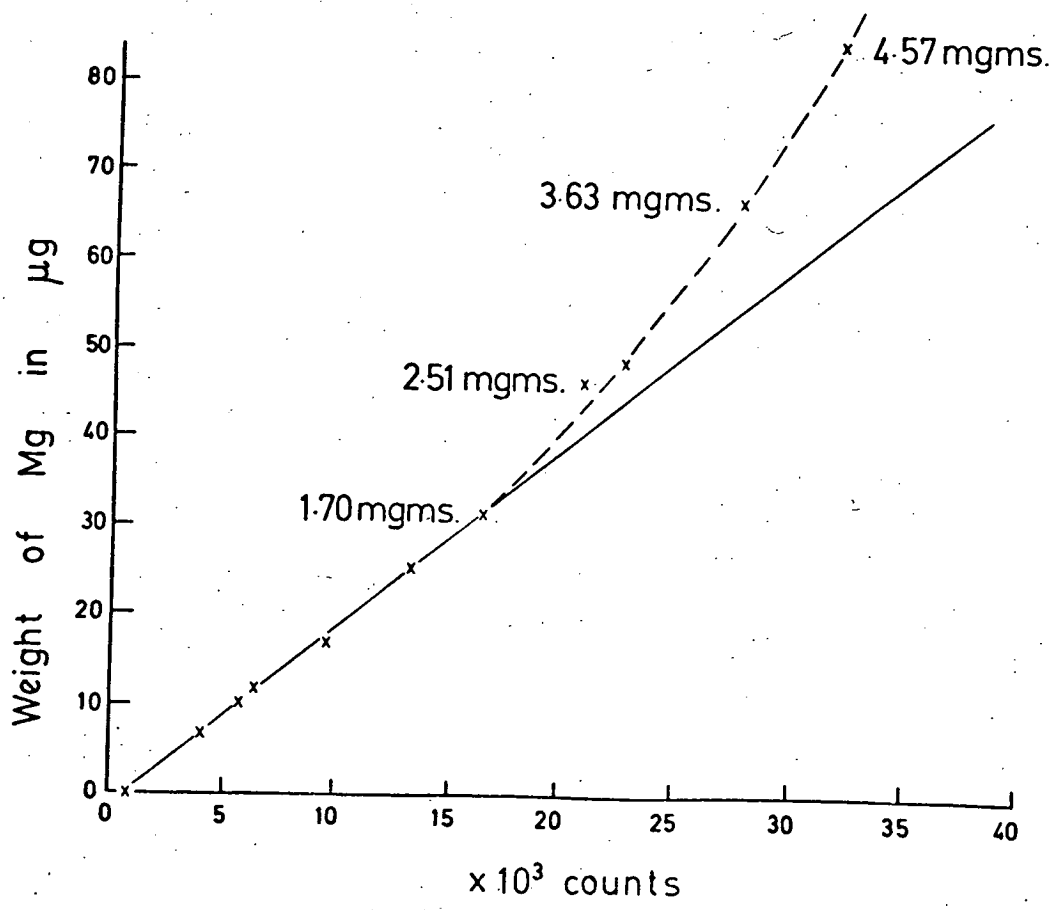
and only that fraction between ~1-5μ was employed for standard preparation. Various amounts (maximum 5mg) of the standards were weighed into glass weighing bottles to which ~20ml of distilled/deionised, membrane filtered water was added. Each bottle was then placed in an ultrasonic cleaning bath ([illegible] ELECTRONICS) in order to homogenise the suspension. The resulting dispersion was transferred quantitatively to a beaker containing ~1l of distilled/deionised, membrane filtered water. This second dispersion was mixed with a glass rod prior to its quantitative filtration through a SARTORIUS membrane filter (p. 96). Finally the filter papers were dried in a desiccator. Despite the matrix variation between the 3 rocks, a linear relationship between spectrometer response and element concentration was obtained except for the lighter elements near the upper limit of the weight range used (i.e. ~5mg).

A second, more comprehensive series of standards was prepared from the manganese-rich siltstone and the greywacké. Fig. C.1 shows that linearity exists between instrument response and K concentration up to 4.5mg at least, whereas there is a divergence from linearity in the case of Mg (the lightest element analysed) above about 2mg. The latter is also true for Al and Si although in the case of P, deviation from linearity is negligible up to 4.5mg. With the exception of the anomalous particulate matter samples collected from the anoxic waters of Bolstadfjord (see p. 41 ; their greatest amount of particulate matter is 4.6mg), the amount of suspended particulate matter collected on each filter paper rarely

Fig. C.1

Calibration graphs for K and Mg analysis in suspended particulate matter





exceeds 2mg. Fortuitously the flow rate of fjord waters through a SARTORIUS membrane filter became so slow when about 2mg of material covered the paper that filtration was generally halted at this stage.

For routine analysis, standards and samples were run in the usual way (p. 109) but with cellulose backing discs. Instrument conditions differed slightly from those indicated in Table C.2 (Ca: tube at 60kV, 24mA; Ti and K: counting time per cycle = 20 seconds; Mn: counting time per cycle = 40 seconds, background used (60.52°); S: tube at 60kV, 24mA, counting time per cycle = 100 seconds, collimator = coarse, background used (73.42°); Cl: tube at 60kV, 32mA, counting time per cycle = 40 seconds, background used (63.10°); as Cl, S and Mn were all analysed with the 1212 spectrometer, the discrimination was automatic and counter EHT = 1700V). Synthetic standards were prepared for Cl (from mercurous chloride), and SU 1 (a Spectroscopy Society of Canada Standard) was employed for S standardization. Straight line calibration curves were plotted manually for all elements and the appropriate parameters fed into a program used to process the data (ERCC facilities). It was necessary to correct the Ca peak intensity for a considerable contribution from the filter paper itself and some other peak intensities for differences in blank values between the three possible sample positions in the spectrometer. A significant loss of S (in the case of samples from the anoxic waters of Bolstadfjord) and a slight loss of Cl were noted with length of time that the samples were subjected to analysis. These two

TABLE C.6

Precision of suspended particulate matter analyses

Element	Analytical Precision	Relative Deviation+ between 1971 and 1972 results*
Al	±1%	±6%
Ca	±20%	±26%
Cl	±20%	
Fe	±4%	±7%
K	±6%	±12%
Mg	±9%	±6%
Mn	±3%	±10%
P	±10%	±22%
S	±1%	±29%
Si	±1%	±8%
Ti	±4%	±10%

* A completely different set of standards were used in 1972.

\+ Relative deviation (%) $= \sqrt{\frac{\Sigma p^2}{2n}}$

where p = difference between each pair of duplicate analyses expressed as a percentage of the mean of the pair; n = number of analyses.

elements were therefore the first to be analysed. The analytical precision (expressed in terms of relative deviation and based on 9 duplicate analyses) and the relative deviation between 1971 and 1972 results (based on 6 duplicate analyses) are shown in Table C.6.

x) Mineralogy of suspended particulate matter

The mineral content of the 1970 and 1971 particulate matter samples was partially identified by X-ray diffraction (see p. 108 for instrument conditions). The filter papers were prepared by sticking a fragment (~1 x 1cm) of each to a glass slide with silicone grease. See p. 32 for criteria used in mineral identification.

xi) Scanning electron microscopy

A S4 STEREOSCAN scanning electron microscope was employed in the partial identification of suspended particulate matter constituents. The work was carried out at the Department of Electrical Engineering under the supervision of J. Goodall.

APPENDIX D

Chemical Analyses

i) Hydrographic and hydrochemical data (see Table D.1)

Density (σ_t) was calculated from the temperature and salinity data following the computation outlined in Knudsen's (1901) 'Hydrographical tables'.

ii) Suspended particulate matter and dissolved metal data (see Table D.2)

The analytical concentrations of S, Mg, Ca and K in suspended particulate matter samples, collected during 1971 and 1972, were corrected for the contribution from retained sea salt as follows:-

$$S = S_{(anal.)} - 0.0465 \times Cl$$

$$Mg = Mg_{(anal.)} - 0.067 \times Cl$$

$$Ca = Ca_{(anal.)} - 0.021 \times Cl$$

$$K = K_{(anal.)} - 0.02 \times Cl$$

The total weight of suspended particulate matter, as determined gravimetrically, is also corrected for retained sea salt:-

$$\text{total weight} = \text{total weight}_{(anal.)} - 1.804 \times Cl$$

iii) Sediment data (see Table D.3)

All the sediment data is salt corrected (see Doff, 1970). The analytical concentrations of S, MgO, CaO, K_2O (in wt.%) and Sr (in ppm) were corrected for the contribution from sea salt as follows:-

$$S = S_{(anal.)} - 0.0465 \times Cl$$

$$MgO = MgO_{(anal.)} - 0.11 \times Cl$$

$$CaO = CaO_{(anal.)} - 0.03 \times Cl$$

$$K_2O = K_2O_{(anal.)} - 0.05 \times Cl$$

$$Sr = Sr_{(anal.)} - 4.21 \times Cl$$

The dilution effect of the salt was accounted for by multiplying all element concentrations by 100/100 - 1.804 x Cl.

The 'Statistical Package for the Social Sciences' (SPSS) (Nie et al., 1970), which is available in the IBM 370/155 computer at the Edinburgh Regional Computing Centre, was employed for all statistical computations (mean, range, correlation coefficients, etc.). Correlation coefficients were calculated using the non-parametric Kendall Rank method (Table D.4).

In Chapter 6, the sediments were divided into five lithological types. The samples included in each group are as follows:-

	Core	Depth (cm)	Number of Samples
1. 'Normal' anoxic sediments (76 samples)	Mo 4(1)S	0-80	8
	Mo 7(2)S	0-130	12
	Mo 8	0-20	4
		40-50	2
	Mo 10	0-41.5	8
	Mo 14	0-45	9
	Mo 49	0-10	3
	Mo 34(2)S	50-80	3
	Bo 1	0-20	6
		22-40.5	2

	Core	Depth (cm)	Number of Samples
'Normal' anoxic sediments (continued)	Bo 1	53.5-90	4
		93-105	2
		106-120	1
	Bo 1A	0-39	5
		46-82	6
	Bo 2	0-21	1
2. Organic poor anoxic sediments (11 samples)	Bo 1	20-22	1
		40.5-53.5	2
		90-93	1
		105-106	1
	Bo 1A	39-46	1
	Bo 2A	24.5-26.5	1
		44.5-46	1
		63.5-65	1
	Bo 6	35-38	1
		80-86	1
3. Shelly anoxic sediments (29 samples)	Mo 8	20-35	3
		50-57.5	2
	Mo 14	45-50	1
	Mo 26	0-75	15
	Mo 34	0-8	3
	Mo 34(2)S	0-50	5

	Core	Depth (cm)	Number of Samples
4. Mn-rich anoxic sediments (37 samples)	Bo 2	21-83	7
	Bo 2A	0-24.5	7
		26.5-44.5	2
		46-63.5	2
		65.5-85	2
	Bo 6	0-80	17
5. Oxic sediments (21 samples)	Mo 22	0-14	7
	Mo 23	0-10	2
	Mo 42	0-10	5
	Mo 44	0-10	2
	Mo 45	0-10	5
	Total		174

TABLE D.1

Hydrographic and hydrochemical data

Station and Date	Depth (m)	S‰	T° C	σ_t	O_2 saturation
Mo 8	0	1.00	4.20	0.84	100.00
1970	1	1.20	3.90	1.00	100.00
	2	9.25	6.40	7.30	100.00
	3	15.30	6.42	12.05	100.00
	4	16.60	6.78	13.04	100.00
	5	19.15	6.81	15.03	98.00
	7	21.40	6.42	16.83	98.00
	9	22.55	6.80	17.70	97.50
	11	23.50	6.80	18.44	99.00
	13	24.50	6.70	19.24	97.00
	15	25.00	6.78	19.62	96.30
	17	26.25	6.75	20.60	92.50
	19	27.40	6.80	21.50	85.50
	21	29.05	6.00	22.89	80.00
	23	30.40	5.20	24.04	65.00
	25	30.80	4.95	24.38	56.50
	30	31.25	4.70	24.76	45.00
	35	31.50	5.18	24.91	37.50
	40	32.10	5.00	25.40	32.00
	45	32.16	5.60	25.38	29.00
	50	32.30	4.80	25.58	25.50
	60	32.30	4.80	25.58	22.50
	70	32.33	4.80	25.61	22.40
	80	32.35	4.80	25.62	24.00
	90	32.37	4.80	25.64	25.50
	100				26.50
	110				28.00
	120				27.50
	130				27.50
	140				28.00
	150				21.80
	160				20.50
	170				20.50

Station and Date	Depth (m)	S‰	T° C	σ_t	O_2 saturation
Mo 23	0	8.78	5.30	6.99	100.00
1970	1	18.93	5.75	14.96	97.00
	2	23.57	5.37	18.64	97.00
	3	26.72	5.25	21.13	92.00
	4	28.89	6.40	22.71	100.00
	5	29.33	6.55	23.04	95.50
	7	29.68	6.50	23.32	100.00
	9	29.97	6.50	23.55	99.00
	11	30.02	6.45	23.60	98.50
	13	30.12	6.55	23.66	99.00
	15	30.17	6.75	23.68	99.50
	17	30.22	6.80	23.71	98.50
	19	30.27	6.45	23.79	98.50
	21	30.42	6.45	23.91	98.25
	23	30.42	6.50	23.90	98.00
	25	30.52	6.55	23.98	98.00
	30	30.62	6.60	24.05	98.00
	35	30.76	6.70	24.15	97.00
	40	30.91	6.80	24.25	97.50
	45	31.01	6.80	24.33	96.00
	50	31.69	6.85	24.86	94.75
	60	31.96	6.75	25.08	86.00
	70	32.94	6.75	25.85	64.50
	80	33.64	6.75	26.40	51.50
	90	34.03	6.85	26.70	47.00
	100				51.50
	110				50.00
	120				50.50
	130				51.00
	140				50.50
	150				51.50
	160				51.00
	170				51.50
	180				54.25
	190				54.50
	200				43.50
	210				42.50

Station and Date	Depth (m)	S‰	T° C	σ_t	O_2 saturation
Mo 7	0	1.32	5.35	1.07	100.00
1970	1	4.67	5.60	3.72	104.00
	2	13.82	5.60	10.95	108.00
	3	19.71	5.62	15.58	105.00
	4	20.42	5.85	16.12	104.00
	5	21.44	5.92	16.91	104.00
	7	22.66	6.00	17.86	102.00
	9	23.57	6.05	18.57	102.00
	11	24.28	6.15	19.12	100.00
	13	24.89	6.21	19.59	97.00
	15	25.45	6.22	20.03	96.50
	17	26.42	6.22	20.79	94.00
	19	28.09	6.25	22.10	86.00
	21	30.38	4.40	24.10	75.00
	23	30.89	4.45	24.50	66.50
	25	31.50	4.40	24.99	59.00
	30	31.95	4.50	25.34	49.00
	35	32.57	4.50	25.83	43.50
	40	32.64	5.16	25.81	40.00
	45	32.78	5.28	25.91	34.50
	50	32.82	5.55	25.91	30.50
	60	32.87	5.75	25.92	30.10
	70	32.92	5.40	26.01	30.50
	80	32.92	3.70	26.19	31.10
	90	32.94	3.95	26.18	31.50
	100				32.10
	110				32.40
	120				33.10
	130				34.00
	140				34.50
	150				34.50
	160				35.20
	170				35.50
	180				35.50
	200				21.00
	210				6.50

Station and Date	Depth (m)	S‰	T° C	σ_t	O_2 saturation
Mo 34	0	10.45	5.27		100.00
1970	1	19.10	5.40		105.00
	2	22.00			100.00
	3	23.50			90.00
	4	25.20			86.50
	5	26.50			88.00
	7	27.40			92.00
	9	28.45			89.80
	11	30.10			89.00
	13	30.40			88.00
	15	30.50			88.00
	17	30.60			86.00
	19	30.70			86.00
	21	30.95			80.00
	23	32.50			57.00
	25	33.85			45.00
	30	33.97			42.20
	35	34.04			39.80
	40	34.09			28.00
	45	34.14			20.20
	50	34.22			20.50
	60	34.24			20.40
	70	34.24			20.20
	80	34.18			20.00
	90	34.16			19.80
	100				19.50
	110				19.40
	120				19.10
	130				18.95
	140				18.80
	150				18.50
	160				18.20
	170				17.60
	180				17.10
	190				16.75
	200				16.30
	210				16.00
	220				15.50
	230				15.00
	240				14.70

Table D.1 continued

Station and Date	Depth (m)	S‰	T° C	σ_t	pH	Eh (mV)	O_2 (ml/l)	
Mo 49 1971	0	1.85	12.57	0.93	6.78	+453		
	1	1.85	12.45	0.95			7.86	
	2	7.00	12.93	4.87	7.29	+473		
	3	10.90	12.93	7.87				
	4	12.40	13.00	9.02				
	5	13.30	12.95	9.72	8.16	+434	8.23	8.21
	7	17.20	12.50	12.79				
	9	19.55	12.25	14.64				
	10				8.09		7.48	7.82
	11	21.20	12.03	15.94				
	13	22.80	11.25	17.30				
	15	24.35	10.25	18.66	7.77	+435	7.27	7.56
	17	27.10	9.05	20.97				
	19	28.15	8.38	21.88				
	21	28.60	8.15	22.26				
	25	29.15	8.00	22.71	7.60	+452	4.70	
	30	29.60	7.93	23.08				
	35	30.40	7.85	23.71				
	40	31.40	7.90	24.49	7.11	+382	1.03	
	45	31.60	7.90	24.64				
	50	31.80	7.95	24.79				
	60	32.00	8.00	24.94	7.26	+456	1.00	
	70	32.10	8.00	25.02				
	80	32.14	8.05	25.05	7.22	+467	0.60	
	90	32.16	8.05	25.06				
	100	32.19	8.05	25.08				
	105				7.19	+467	0.76	
	110	32.20	8.05	25.09				
	115	32.10	8.15	25.00				
	120	32.10	8.15	25.00	7.23	+447	0.68	
	130				7.25	+402	1.15	
	140				7.24	+462	0.74	
	150				7.23	+437	0.58	
	160				7.18	+462	0.79	
	170				7.23	+462	0.78	
	180				7.21	+427	0.63	
	200				7.24	+447	0.20	
Bo 2 1971	0	1.40	13.60	0.45	6.52	+348	7.79	
	1	1.40	13.45	0.47				
	2	1.40	13.35	0.48				
	3	1.40	13.20	0.50				
	4	1.40	13.15	0.51				
	5	1.40	13.15	0.51				
	7	1.40	13.00	0.53				
	9	1.40	12.85	0.55				
	10				6.55	+413	8.28	
	11	1.45	12.70	0.60				
	13	1.55	12.60	0.69				
	15	1.60	12.40	0.76				
	17	1.75	12.40	0.87				
	19	2.25	12.85	1.20				
	20				7.21	+407	6.47	
	21	3.25	10.35	2.27				
	23	12.90	7.10	10.11				
	25	16.00	6.60	12.58				
	27	19.20	6.50	15.10				
	30	19.75	6.45	15.54	7.00	+398	3.85	
	35	20.05	6.20	15.80				
	40	20.35	5.85	16.06	7.11	+398	4.65	
	45	20.65	5.85	16.30				
	50	20.70	5.85	16.34	7.06	+388	3.97	
	60	20.95	5.85	16.53	6.98	+399	3.21	
	70	21.15	5.85	16.70	6.79	+389	1.80	
	80	21.20	5.85	16.73	6.76	+388	1.80	
	90	21.25	5.85	16.77	6.79	+394	2.91	
	100	21.30	5.85	16.81	6.73	+394	1.00	
	110	21.35	5.85	16.85	6.63	+393	0.70	
	115	21.35	5.85	16.85				
	118				6.68	+388	0.70	
	120	21.25	5.85	16.77				
	123						1.00	
	124				6.69	+389	0.40	
	127						0.70	
	129						1.80	

Table D.1 continued

Station and Date	Depth (m)	S‰
Bolstadfjord - inner threshold 1971	0	1.60
	2	1.60
	5	1.75
	7	1.75
	9	2.40
	11	2.30
	12	2.70

Station and Date	Depth (m)	T° C	S‰	σ_t
Stamneshella Harbour 1971	0	13.40	6.10	4.10
	1	13.40	6.50	4.41
	2	13.25	9.60	6.82
	3	12.80	28.60	21.51
	4	12.35	30.00	22.67
	5	12.00	30.50	23.12
	7	11.40	31.00	23.62
	9	11.00	31.20	23.84
	11	10.70	31.40	24.05
	15	10.25	31.80	24.44
	20	9.80	32.29	24.89
	25	9.40	32.75	25.32
	30	8.80	33.70	26.15
	35	8.50	33.98	26.42
	40	8.25	34.31	26.72

Station and Date	Depth (m)	S‰	T° C	σ_t	pH	Eh (mV)	O_2 ml/l	$E_{S^=}$ (mV)	$pS^=$
Bo 3 1971	42.5				6.82	+258	3.05	-510	14.31
	45.0				6.81	+388	3.12	-440	17.06
	47.5				6.77	+279	1.80	-520	13.92
	50.0				6.65	+298	0.70	-520	13.92
	52.5				6.77	+113	0.70	-540	13.06
	55.0				6.69	+43	0.20	-560	12.29
	57.5				6.70	+43	-	-570	11.90
	60.0				6.70	+18	-	-580	11.52
	65.0				6.68	-3	-	-580	11.52
	70.0				6.67	-2	-	-590	11.14
	78.0				6.68	+13	-	-590	11.14
Bo 1 1971	0	1.02	12.30	0.30	5.98	+553	7.53	-455	16.47
	1	1.02	12.30	0.30					
	2	1.02	12.30	0.30					
	3	1.02	12.30	0.30					
	4	1.02	12.30	0.30					
	5	1.02	12.30	0.30	6.43	+309	7.72	-470	15.88
	6	1.02	12.30	0.30					
	7	1.02	12.30	0.30					
	8	1.02	12.30	0.32					
	9	1.02	12.20	0.32					
	10	1.02	12.20	0.32	6.21	+384	7.47	-560	12.29
	11	1.02	12.20	0.32					
	12	1.02	12.15	0.32					
	13	1.02	12.05	0.33					
	14	1.07	12.05	0.37					
	15	1.07	12.05	0.37	6.67	+314	7.99	-480	15.49
	16	1.12	12.00	0.42					
	17	1.12	12.00	0.42					
	18	1.28	11.75	0.60					
	19	1.63	11.63	0.89					
	20	2.04	11.20	1.25	6.81	+386	7.38	-565	12.10
	22	3.77	8.30	2.84	7.13	+358	7.12	-505	14.50
	23	11.32	6.45	8.91					
	24	14.40	5.95	11.38					
	25	15.90	5.85	12.57	6.96	+219	5.99	-450	16.67
	27	19.35	5.80	15.28					
	29	20.65	5.75	16.31					
	30				6.86	+322	3.53	-570	11.90
	31	20.80	5.60	16.44					
	33	20.90	5.60	16.52					
	35	21.00	5.50	16.60	6.71	+193	3.42	-525	13.73
	40	21.10	5.40	16.69	6.62	+318	3.93	-570	11.90
	45	21.20	5.30	16.78		+236			
	50	21.40	5.30	16.94	6.65	+298	0.70	-600	10.75
	55	21.50	5.35	17.01	6.66	+93	0.20	-620	9.99
	60	21.70	5.40	17.16	6.66	+18		-640	9.22
	65	21.75	5.40	17.20	6.61	-67		-610	10.37
	70	21.85	5.40	17.28	6.63	-37		-630	9.60
	75	21.85	5.37	17.28	6.61	-67		-620	9.99
	80	21.85	5.35	17.29	6.65	-38		-630	9.60
	83	21.85	5.35	17.29					
	84	21.85	5.35	17.29					

Table D.1 continued

Station and Date	Depth (m)	S‰	T° C	σt	Percentage O_2 saturation	Phosphate (µg at./l)	Silicate (µg at./l)	H_2S (µg at./l)	Titration alkalinity (m equivs./l)
Bo 5	0	1.10	14.95	0.02	100.0				
1972	1				100.0				
	2	1.10	14.50	0.09	100.0				
	3				100.0				
	4	1.10	14.20	0.13	99.8				
	5				98.5	0.06	16.48		
	6	1.40	13.30	0.49					
	10	2.10	11.25	1.28	96.0		13.90		
	15	3.30	10.20	2.32	95.0	0.03			
	17	4.80	8.00	3.69					
	18				86.0				
	19	12.20	4.60	9.73					
	20				78.5				
	21	15.80	3.00	12.65					
	22				79.0				
	23	16.30	2.95	13.05					
	25	16.50	2.90	13.21	75.5				
	30	17.25	3.00	13.80	71.0				
	35	20.55	3.55	16.39	50.5				
	37				48.0				
	40	20.95	3.60	16.70	45.5	0.26	24.59		
	50	21.30	3.60	16.98		0.07	34.07		
	55	21.35	3.62	17.02		0.33	21.09		
	60	21.45	3.65	17.10		0.20	28.91		
	65					0.42	29.28		
	70	21.55	3.70	17.17		0.44	20.50		
	75					0.17	44.84		
	80	21.55	3.65	17.18		1.15	44.94		
Bo 6	45					0.20	27.99		
1972	47.5					0.32	28.54		
	50					0.14	25.87		
	55					0.33	27.26		
	57.5					1.31	55.43		
	60					1.77	59.30		
Bo 4	0	1.10	14.10	0.14	100.0	0.39	9.20		
1972	1				100.0				
	2	1.10	14.00	0.16					
	3				100.0				
	4	1.10	14.05	0.15					
	5				100.0	0.11	11.90		
	6	1.20	13.35	0.33					
	7				100.0				
	8	1.50	12.20	0.70					
	10	2.10	10.65	1.34	98.0	0.01	12.50		
	15	3.30	10.05	2.34	96.5	0.28	12.10		0.1939
	17				95.0				
	18	6.30	6.75	4.95	91.0				
	19	7.50	4.60	6.00	87.0				
	20	14.15	3.75	11.31	80.0	0.17	18.50		1.0832
	21				82.0				
	22	15.80	2.60	12.66					
	23	16.10	2.60	12.90	80.5				
	25	16.35	2.60	13.10	77.0	0.15	17.90		1.0312
	30	17.30	2.80	13.85	74.0	0.48	22.00		1.1355
	32	17.80	2.95	14.24					
	34	18.80	3.10	15.03					
	35				53.0	0.30	18.60		
	36	20.80	3.25	16.61					
	40	21.00	3.30	16.76	49.0	0.30	22.90		1.4515
	42.5					0.58	22.90		
	45					0.40	27.80		
	47					0.23	34.70		
	49					0.61	33.50		1.5937
	50	21.35	3.40	17.03					
	51					0.93	35.50	12	
	52.5					0.79	39.30	7	
	53					0.78	32.60	11	
	55	21.40	3.40	17.07		0.77	34.70	33	1.7565
	57					1.13	43.90	64	
	59	21.60	3.50	17.22		1.52	48.20	100	2.1575
	62.5					2.31	53.80	114	
	65					2.26	57.30	111	
	67.5					2.45	62.60	157	
	70	21.65	3.60	17.26		2.35	61.40	134	2.2450
	72.5					2.84	60.80	174	
	75					2.83	60.80	193	2.2701
	80	21.65	3.60	17.26					

TABLE D.2

Suspended particulate matter and dissolved metal data

Station and Date	Depth (m)	Suspended particulate matter (µg/l) Ca	K	Fe	Ti	Si	Al	Mg	P	Mn	S	Cl	Total weight	Dissolved metals (µg/l) Mn	Fe	Ni	Cu	Zn
Mo 7 1970	0	2.67	8.33	16.89	1.20	73.33	16.50	5.00	3.93	0.20				1.82	3.05	1.07	0.81	14.38
	10	5.18	7.11	16.92	0.15	23.86	2.03	4.21	1.95	0.20				1.34	7.25	0.90	2.10	25.19
	20	2.75	6.25	15.81	n.d.	30.30	1.36	1.42	1.61	n.d.				0.34	0.95	0.72	0.16	2.23
	30	1.23	5.04	13.68	n.d.	15.35	n.d.	2.85	1.18	n.d.				0.27	7.24	n.d.	n.d.	4.25
	40	1.33	2.50	5.56	n.d.	10.83	0.67	0.92	0.57	0.40				0.24	2.63	n.d.	n.d.	
	60	4.04	5.42	19.01	0.74	21.42	0.79	0.74	1.26	2.10				1.03	11.73	1.59	0.35	6.04
	100	3.10	3.75	10.00	n.d.	5.13	n.d.	1.50	0.88	2.55								
	140	2.01	5.03	19.43	n.d.	8.04	2.02	1.51	1.48	6.50				3.11	2.75	n.d.	n.d.	2.31
	180	2.00	0.50	13.00	n.d.	6.50	n.d.	0.83	1.05	14.20				2.59	4.43	n.d.	n.d.	
	210	3.70	2.83	10.78	n.d.	6.67	0.50	1.89	1.17	55.35				6.01	4.94	0.25	2.13	3.88
Mo 23 1970	0	1.47	2.70	7.33	0.38	29.33	5.33	1.93	2.10	0.12				1.52	2.45	1.94	0.46	9.50
	10	2.56	2.35	2.38	0.03	8.93	1.07	2.20	0.98	0.16				0.00	1.02	n.d.	0.38	3.51
	30	2.13	2.46	2.75	0.08	10.63	2.00	2.05	0.79	0.17								
	50	0.73	1.35	3.35	0.15	14.00	2.88	1.45	0.85	0.15				0.04	2.60	n.d.	0.94	5.40
	100	2.25	2.40	3.00	0.10	12.13	2.38	1.85	0.64	0.26								
	150	0.85	1.73	4.50	0.26	18.88	4.18	1.90	0.71	0.16								
	200	10.35	5.95	13.00	0.75	53.50	12.00	-	1.46	0.43				0.47	8.02	1.25	1.10	3.64
Bo 5 1972	0	2.10	2.85	11.65	0.37	23.23	8.01	1.88	10.79	0.41	9.30	0.29						
	5	2.72	4.04	14.46	0.93	34.97	12.94	3.03	11.98	0.56	11.51	0.29						
	10	1.74	3.99	14.15	0.54	35.49	12.16	3.52	8.50	0.62	8.62	0.38						
	15	1.88	2.29	13.67	0.60	32.10	11.25	2.34	8.13	0.68	0.68	0.59						
	40	1.64	2.26	7.57	0.43	27.89	5.08	2.01	4.18	0.39	4.72	2.98						
	45	1.84	2.49	8.60	0.57	36.76	9.02	2.36	4.33	1.86	4.97	3.72						
	50	1.15	1.78	8.37	0.40	22.61	6.11	1.66	5.25	1.96	5.90	0.38						
	55	1.95	2.30	8.51	0.61	30.31	7.81	1.85	4.78	2.82	4.62	1.64						
	60	2.27	2.49	26.83	0.49	21.93	7.03	1.56	7.76	0.33	9.69	3.42						
	65	1.92	3.61	10.14	0.60	36.58	8.13	2.59	7.04	0.59	6.12	0.47						
	70	2.04	2.29	5.73	0.33	23.82	5.39	1.62	5.19	1.53	5.46	4.06						
	80	1.95	2.48	236.29	0.86	28.33	10.82	5.67	43.30	0.10	143.58[x]	9.36						
Bo 6 1972	47.5	1.83	2.77	7.89	0.56	33.96	6.81	2.09	3.67	0.43	4.59	0.94						
	50	1.64	1.84	10.06	0.50	30.75	6.74	1.74	4.93	0.60	5.10	0.34						
	55	2.17	4.24	11.71	0.62	32.63	7.42	2.91	6.84	1.01	7.09	6.45						
	57.5	1.35	1.99	292.02	0.57	18.03	9.17	2.01	53.03	0.08	780.33[x]	7.01						
	60	1.42	2.02	285.48	0.62	18.24	9.41	2.02	57.12	0.04	1305.13[x]	9.26						
River Vosso 1972		1.84	3.40	16.14	0.79	31.28	12.97	2.01	17.21	0.48	12.62	1.00						

n.d. not detectable
\- not determined

x anomalous S concentrations

Table D.2 continued

Station and Date	Depth (m)	Suspended particulate matter (µg/l) Ca	K	Fe	Ti	Si	Al	Mg	P	Mn	S	Cl	Total+ weight	Dissolved metals (µg/l) Mn	Fe	Ni	Cu	Zn
No 49	0	0.89	3.07	9.46	0.48	27.83	24.49	1.95	4.09	0.22	5.96	0.83	377	3.54	13.22	1.51	1.44	11.21
1971	0(B)	1.29	2.67	7.81	0.42	25.73	21.50	1.68	1.70	0.13	5.02	0.95	473					
	2(B)	1.49	2.36	7.85	0.37	22.94	18.14	1.66	1.77	0.00	5.12	1.00	454					
	5	7.37	9.26	23.12	1.44	209.91	19.47	5.80	13.12	0.60	12.80	1.30	708					
	5(B)	1.92	3.55	10.92	0.54	58.95	9.48	2.36	4.59	0.36	4.31	1.48	362					
	10	5.50	3.10	6.51	0.29	36.54	5.21	2.22	5.16	0.35	6.06	3.43	455	1.18	2.44	0.19	0.02	n.d.
	10(B)	3.86	3.61	7.08	0.46	63.58	6.82	1.76	4.83	0.33	2.19	1.90	459					
	15	3.02	2.06	2.27*	0.18	17.14	2.98	1.23	2.07	0.18*	2.80*	2.60*	490					
	25	1.68	1.85	0.95*	0.07	9.62	1.34	0.88	2.59	0.09*	2.19*	5.96*	260	0.75	2.15	n.d.	1.03	3.50
	40	2.21	1.61	4.39	0.11	13.37	2.29	0.54	0.70	1.75	2.15	13.65	436					
	60	1.79	1.88	8.39	0.32	16.08	3.21	2.21	3.78	1.17	3.93	10.99	359					
	80	2.95	1.51	8.94	0.28	13.85	3.09	2.97	1.16	0.32	2.90	6.63	438					
	105	2.71	1.47	8.35	0.24	10.41	2.88	0.68	0.98	0.65	3.03	6.23	429					
	120	2.01	1.94	5.43	0.13	7.25	1.52	0.63	3.56	0.67	2.79	14.78	332					
	130	1.55	1.16	7.69	0.16	7.10	1.76	0.44	0.97	1.03	1.35	6.84	300					
	140	1.69	1.49	6.36	0.14	7.51	1.87	0.38	2.51	1.72	2.27	9.96	256	9.09	5.56	0.31	0.65	3.59
	150	1.19	1.19	7.12	0.12	4.85	1.17	0.25	2.64	0.71	2.16	8.99	250					
	160	2.03	1.27	7.71	0.16	9.46	2.20	0.62	1.31	2.22	2.36	11.86	443					
	170	2.18	1.33	7.54	0.04	2.62	1.00	0.01	1.39	2.23	3.94	18.17	427					
	180	1.76	1.24	16.06	0.17	7.68	1.92	0.79	2.86	2.00	1.93	10.74	404	46.20	7.40	0.34	1.28	5.64
	200	3.33	1.33	12.06	0.15	6.45	1.81	0.71	1.55	33.73	3.75	15.76	516					
	210	13.56	3.49	12.95	0.14	3.91	1.64	2.71	5.21	148.79	9.18	53.92	1485	245.00	16.80	n.d.	0.48	9.35
River Moelv 1971		1.94	1.50	5.80	0.33	15.33	10.36	0.79	1.11	0.06	4.80	0.14	325	2.68	5.18	2.10	n.d.	5.27
River Beitleelv 1971		0.08	0.69	1.29	0.09	7.66	2.35	0.13	2.68	0.00	2.07	0.04	59					
No 1	0	0.86	3.92	21.76	0.66	43.17	18.44	2.45	7.91	1.15	8.70	0.23	599					
1971	5	2.23	3.47	19.68	0.49	39.06	17.03	2.06	4.30	0.87	7.72	0.55	777	4.66	11.20	0.68	0.70	3.60
	10	2.21	4.24	19.37	0.57	36.77	15.69	2.40	7.30	0.81	6.31	0.43	399					
	15	2.70	3.40	18.31	0.48	39.85	15.55	2.26	3.46	0.84	6.09	0.53	666					
	20	5.08	6.66	34.81	1.62	74.55	25.18	10.12	5.38	1.58	6.05	4.64	844	7.86	18.25	n.d.	2.85	42.80
	22.5	2.34	3.13	12.44	0.41	35.05	12.53	2.07	1.90	0.82	3.37	2.73	498					
	25	2.56	3.56	13.32	0.46	37.80	12.98	2.44	1.92	1.01	4.89	5.31	581					
	30	-	-	-	0.70	37.75	11.87	-	3.36	-	-	-	532					
	35	1.35	2.47	6.67*	0.25	22.17	8.15	1.46	3.10	3.04*	1.58*	4.22*	364					
	40	1.14	2.56	12.59	0.45	25.17	9.73	1.69	3.35	6.76	2.74	4.65	331	1.70	7.60	0.60	1.40	7.00
	50	2.03	2.58	12.39	0.25	16.82	7.16	1.39	5.23	21.92	2.08	5.81	506	133.00	3.00	n.d.	0.50	0.70
	55	1.38	1.76	17.79	0.20	13.93	5.79	1.22	6.87	0.15	10.56x	3.38	329	740.00	27.80	n.d.	0.30	1.40
	60	0.98	2.33	9.46	0.26	17.82	6.63	1.75	4.14	0.07	479.43x	3.17	737	740.00	300.00	0.10	0.60	3.20
	65	0.54	1.86	12.27	0.25	18.32	7.37	1.83	3.38	0.07	1342.09x	2.10	1383	670.00	265.00	0.80	0.90	2.40
	70	0.48	1.94	13.11	0.23	14.69	6.17	0.89	3.72	0.07	556.27x	2.57	817					
	75	0.50	1.12	7.16	0.08	11.96	5.31	1.32	1.75	n.d.	1939.42x	1.89	1926					
	80	0.04	1.93	13.09	0.30	17.27	7.06	0.96	4.18	0.12	1242.82x	0.31	1171	580.00	180.00	n.d.	1.20	5.70

n.d. not detectable
\- not determined
* filter paper disintegrated during analysis
\+ salt corrected
x anomalous S concentrations

Table D.2 continued

Station and Date	Depth (m)	Suspended particulate matter (µg/l) Ca	K	Fe	Ti	Si	Al	Mg	P	Mn	S	Cl	Total+ weight	Dissolved metals (µg/l) Mn	Fe	Ni	Cu	Zn
Bo 2	0	1.68	4.11	20.24	0.67	45.01	17.65	2.18	13.07	0.68	9.46	0.60	385	4.55	12.32	1.63	1.25	11.22
1971	10	0.56	3.68	18.84	0.50	42.93	17.67	1.94	8.03	0.77	8.05	0.39	308					
	20	1.81	3.08	10.84	0.37	31.05	10.65	1.80	3.55	0.97	4.74	3.23	240	1.23	5.77	n.d.	0.10	2.69
	30	1.31	2.27	6.70	0.23	18.18	6.08	0.85	3.23	1.60	2.86	5.16	212					
	40	1.44	2.33	5.96	0.32	18.33	6.33	0.85	2.77	2.50	4.07	14.86	345					
	50	0.90	1.57	4.74	0.15	12.91	4.73	0.67	4.42	2.23	2.57	3.78	189	1.77	2.22	n.d.	n.d.	3.31
	60	0.72	1.89	6.52	0.18	14.95	5.97	0.85	3.01	3.26	2.99	5.45	147					
	70	0.83	1.81	6.53	0.17	13.45	5.67	0.94	2.69	6.90	3.03	7.52	301					
	80	0.67	1.98	8.40*	0.18	14.49	5.46	0.97	3.17	9.21*	2.83*	6.43*	273	12.25	1.65	0.29	n.d.	5.56
	90	1.31	2.48	12.79	0.19	13.60	5.23	1.03	3.45	8.08	2.14	7.20	304					
	100	1.33	1.96	14.83	0.19	12.50	4.81	0.90	3.10	11.90	3.69	9.36	462					
	110	2.46	1.94	54.59	0.16	10.55	3.98	1.20	4.99	30.50	4.23	9.38	326	95.90	3.75	0.62	1.25	2.20
	118	2.50	1.46	21.85	0.22	10.17	4.04	0.75	1.78	47.41	2.45	2.38	354					
	123	2.26	1.69	19.18	0.12	8.31	3.26	1.04	3.42	40.42	2.67	7.71	203	25.60	3.40	n.d.	0.78	2.75
	127	3.19	2.07	18.54	0.14	9.37	3.51	1.16	1.55	56.87	3.03	16.13	451					
	130	4.97	2.08	17.95	0.15	10.02	3.77	1.61	3.44	103.17	3.39	7.02	431					
River Vosso	1971	1.16	3.92	17.41*	0.43	37.47	14.95	2.08	7.88	0.95*	4.69*	0.29*	239	3.87	16.45	3.21	0.88	6.31
Bo 3	42.5	1.38	2.88	11.03*	0.33	22.47	9.56	1.43	3.61	10.27*	3.13*	4.83*	376	2.60	1.80	n.d.	0.40	3.50
1971	45	1.77	2.97	9.43	0.27	18.82	7.98	1.41	3.41	9.78	2.73	4.88	400	4.30	1.60	n.d.	1.10	3.60
	47.5	3.27	3.30	14.92	0.59	24.37	9.80	1.93	3.53	15.32	5.19	8.53	407	6.40	10.00	0.40	2.30	10.30
	50	5.65	3.33	19.25	0.52	24.35	10.23	2.06	4.59	23.83	6.57	3.16	391	310.00	5.80	0.20	2.30	10.00
	52.5	4.31	4.26	27.08	1.22	33.82	12.77	3.19	7.64	3.22	16.11x	7.55	670	590.00	24.00	n.d.	3.90	8.10
	55	2.69	2.94	23.21	0.59	26.67	9.86	1.75	7.43	0.16	111.38x	2.23	615	710.00	160.00	n.d.	1.20	4.50
	57.5	1.58	2.67	9.81	0.34	17.38	7.05	1.64	4.07	0.02	321.92x	5.01	659	700.00	330.00	n.d.	1.50	2.60
	60	1.83	2.99	16.97	0.63	28.22	9.78	2.40	3.55	0.09	540.94x	3.05	953	650.00	300.00	n.d.	1.70	4.70
	65	5.54	2.83	20.93	0.50	22.60	8.62	1.78	3.55	0.17	181.21x	4.38	854	570.00	230.00	n.d.	1.80	5.50
	70	0.40	1.60	14.51	0.26	14.61	5.92	1.13	4.57	0.05	646.47x	0.11	742	560.00	220.00	n.d.	3.10	10.70
	78	1.34	2.38	12.35	0.31	17.45	6.80	1.41	3.53	0.04	13.24x	5.04	453	530.00	195.00	n.d.	0.20	1.50
Mo 8	0	n.d.	6.13	6.29	0.76	42.45	19.34	4.15	1.60	0.40				4.71	12.74	4.65	4.25	124.10
1970	10	4.76	7.14	15.86	0.14	22.84	2.38	2.85	1.86	0.20				1.11	5.80	2.57	0.56	7.68
	20	3.98	6.55	14.11	n.d.	16.13	2.02	3.28	1.46	0.30				0.55	4.91	2.22	0.41	3.79
	50	n.d.	n.d.	12.69	n.d.	18.79	n.d.	0.64	1.36	0.35				0.83	8.15	1.44	2.41	5.49
	100	n.d.	2.98	12.13	n.d.	7.66	n.d.	0.31	2.30	n.d.				11.13	8.49	n.d.	n.d.	8.93
	150	n.d.	2.34	14.02	n.d.	5.61	1.87	0.33	1.83	0.20				13.70	10.63	n.d.	n.d.	5.01
River Moelv	1970	0.65	5.42	17.16	0.57	32.26	14.52	2.42	1.11									
River Moelv	1970	0.84	3.49	11.95	0.46	25.80	6.14	2.39	1.23					3.05	5.62	1.40	0.54	9.61

n.d. not detectable
* filter paper disintegrated during analysis
\+ salt corrected
x anomalous S concentrations

Table D.2 continued

Station and Date	Depth (m)	Suspended particulate matter (µg/l) Ca	K	Fe	Ti	Si	Al	Mg	P	Mn	S	Cl	Total weight	Dissolved metals (µg/l) Mn	Fe	Ni	Cu	Zn
Bo 4 1972	0	0.46	2.81	10.99	0.35	24.66	8.61	1.75	9.73	-	8.27	0.74						
	5	0.68	3.10	11.89	0.49	24.87	9.44	1.88	10.94	0.28	9.04	1.18						
	10	4.59	5.21	13.64	0.63	36.27	13.70	4.35	10.15	0.70	8.61	3.50						
	15	2.74	4.96	17.23	0.79	40.18	13.06	2.87	13.69	1.30	13.08	1.79						
	20	2.85	4.51	11.65	0.77	33.20	11.13	3.16	10.96	0.91	9.44	4.85						
	25	1.82	3.44	10.23	0.64	34.02	9.60	2.70	7.25	1.96	6.94	3.00						
	30	2.31	4.64	12.56	0.49	27.28	6.82	1.99	8.90	1.70	9.43	7.31						
	35	2.95	8.54	12.64	0.82	48.08	9.12	3.77	25.41	0.80	20.17	16.39						
	40	3.90	5.23	15.34	1.02	45.88	11.18	3.11	11.18	0.47	11.77	7.72						
	42.5	4.07	6.36	12.64	1.00	37.96	9.18	3.15	15.10	0.40	12.92	11.23						
	45	2.27	5.05	13.55	0.83	40.84	10.92	3.95	8.32	-	6.66	4.36						
	47	1.53	3.29	18.36	0.72	33.21	10.21	2.56	7.53	2.89	6.33	4.61						
	49	3.50	4.37	16.83	0.68	29.14	8.50	3.60	10.56	0.56	12.31	9.31						
	51	1.74	2.55	116.42	0.45	17.80	7.55	2.34	26.63	0.09	29.67	12.94						
	52.5	1.69	2.69	88.52	0.64	21.64	8.86	2.36	18.54	0.17	22.69	8.26						
	53	1.54	1.92	81.24	0.52	20.89	7.55	1.38	17.32	0.37	21.38	4.72						
	55	1.09	1.87	65.75	0.35	16.32	6.63	1.77	17.26	0.28	35.88	5.98						
	57	2.30	2.73	130.11	0.56	18.32	8.71	3.03	35.19	0.18	80.23	8.28						
	59	0.99	2.53	188.20	0.85	24.02	11.28	2.25	46.88	0.03	1337.08	2.04						
	62.5	n.d.	1.44	9.72	0.37	17.37	6.25	1.96	5.50	-	1442.87	1.20						
	65	1.33	2.04	253.10	0.66	17.00	9.66	2.05	57.24	0.12	1790.30	8.62						
	67.5	0.50	2.24	15.83	0.94	22.52	9.38	2.49	5.11	n.d.	1749.68	2.14						
	70	n.d.	1.32	8.30	0.37	15.74	5.72	2.03	6.24	n.d.	1945.30	0.22						
	72.5	0.31	2.27	8.78	0.36	17.67	6.63	2.83	6.34	n.d.	1858.57	3.67						
	75	2.80	3.50	14.90	0.66	27.56	9.57	3.00	6.27	n.d.	2119.18	8.28						

n.d. not detectable
- not determined

TABLE D.3

Chemical composition of sediments

Station and Date	Depth (cm)	Major elements (in wt.%)													Trace elements (in ppm)								
		CaO	K_2O	Fe_2O_3	TiO_2	SiO_2	Al_2O_3	MgO	P_2O_5	MnO	S	Total C	CO_2	Organic C	Rb	Zr	Sr	Y	Nb	Pb	Cu	Zn	Ni	Mo
Mo 22 1970	0- 2	4.02	3.45	6.32	0.81	53.80	13.64	2.17	0.27	0.07	0.08	3.28	1.46	2.88	138	161	337	42	14	62	28	145	32	12
	2- 4	3.81	3.36	6.85	0.77	52.01	13.31	2.12	0.25	0.07	0.09	3.13	1.07	2.84	142	194	339	42	17	53	26	135	31	11
	4- 6	3.85	3.38	6.51	0.79	54.02	13.83	1.96	0.27	0.07	0.13	3.01	1.00	2.74	142	186	345	46	14	48	22	123	31	6
	6- 8	4.07	3.59	6.61	0.80	55.69	14.29	2.32	0.27	0.07	0.20	2.81	0.84	2.59	154	193	347	48	19	29	22	119	32	6
	8-10	4.07	3.55	6.52	0.79	55.64	14.54	2.45	0.30	0.07	0.17	2.49	1.22	2.16	151	181	351	50	18	32	19	117	31	8
	10-12	4.03	3.58	6.39	0.78	54.22	14.03	2.26	0.26	0.08	0.28	2.40	0.95	2.15	143	180	355	46	18	30	24	123	33	10
	12-14	3.99	3.55	6.99	0.77	54.33	13.38	2.11	0.24	0.07	0.20	2.38	1.14	2.07	152	181	354	47	17	30	24	122	32	11
Mo 42 1970	0- 2	4.10	3.36	6.40	0.86	54.91	13.68	2.20	0.27	0.07	0.07	2.26	1.03	1.98	139	197	362	47	16	49	24	137	33	7
	2- 4	4.09	3.42	6.40	0.85	55.78	14.20	2.22	0.26	0.07	0.10	2.66	1.10	2.36	139	207	356	42	21	49	22	120	31	11
	4- 6	4.46	3.47	6.50	0.85	56.59	14.89	2.27	0.32	0.07	0.22	2.12	1.17	1.80	134	199	369	53	18	24	20	113	32	8
	6- 8	4.83	3.50	6.70	0.84	55.90	14.74	2.48	0.28	0.07	0.26	2.16	1.66	1.70	140	185	380	44	21	27	23	117	33	12
	8-10	6.04	3.50	6.33	0.81	55.54	14.38	2.44	0.29	0.08	0.25	2.40	2.61	1.68	142	177	431	43	18	20	19	115	31	11
Mo 45 1970	0- 2	4.64	3.58	6.34	0.79	57.79	14.35	2.11	0.25	0.35	0.17	2.07	1.78	1.58	142	200	386	41	15	48	28	139	33	10
	2- 4	4.78	3.54	6.85	0.77	53.57	13.89	2.51	0.26	0.31	0.08	2.59	1.97	2.06	155	161	364	44	15	72	33	169	41	11
	4- 6	5.03	3.71	7.26	0.78	52.74	14.02	6.64	0.23	0.20	0.08	2.80	1.97	2.27	151	164	354	42	15	56	30	149	41	11
	6- 8	5.20	3.58	7.07	0.79	52.04	13.84	2.55	0.27	0.24	0.15	2.74	2.80	1.98	151	161	356	48	16	40	30	134	41	9
	8-10	5.21	3.48	7.05	0.78	50.43	13.49	2.34	0.23	0.27	0.18	2.58	2.38	1.93	152	163	372	44	12	30	29	132	40	9
Mo 23 1970	0- 5	4.44	3.34	5.49	0.73	52.69	13.85	2.10	0.28	0.05	0.12	3.56	1.46	3.16	127	202	368	43	14	51	18	129	28	0
	5-10	4.72	3.47	6.04	0.83	58.16	14.60	2.43	0.33	0.06	0.27	2.81	1.27	2.46	122	198	360	41	16	39	13	105	26	4
Mo 44 1970	0- 5	5.67	3.53	6.99	0.79	54.48	14.33	2.97	0.32	0.43	0.25	2.64	2.14	2.06	132	184	382	38	9	44	25	132	37	13
	5-10	4.33	3.56	7.39	0.78	54.32	14.70	2.79	0.29	0.42	0.24	2.21	1.65	1.76	143	173	336	40	15	34	22	133	41	4
Anoxic sediments																								
Mo 34 (2)S 1970	0-10	8.80	2.24	5.75	0.62	44.71	9.66	1.58	0.24	0.05	2.54	9.25	4.87	7.93	83	150	431	36	11	41	25	105	30	98
	10-20	9.62	2.41	5.43	0.61	46.42	10.18	1.54	0.25	0.06	1.97	6.83	4.96	5.47	92	163	509	42	11	23	29	100	30	87
	20-30	8.49	2.25	6.17	0.61	44.31	9.68	1.35	0.27	0.06	3.01	8.88	3.79	7.84	78	146	413	39	7	20	29	98	32	118
	30-40	7.77	2.38	6.09	0.62	43.92	10.18	1.80	0.28	0.07	2.70	8.67	3.40	7.75	92	148	410	41	17	16	32	114	34	119
	40-50	6.87	2.90	5.83	0.69	49.12	10.84	1.88	0.27	0.09	1.96	6.65	3.12	5.80	113	175	402	43	13	21	28	115	33	73
	50-60	4.77	3.81	6.88	0.76	51.32	13.91	2.53	0.27	0.10	1.36	4.43	1.61	3.99	168	116	338	37	15	23	35	142	36	39
	60-70	4.53	3.90	6.83	0.80	52.97	14.03	2.70	0.27	0.10	1.22	2.99	1.28	2.64	163	129	351	43	18	13	32	135	35	36
	70-80	4.67	3.80	6.76	0.80	53.74	14.37	2.58	0.25	0.10	1.20	3.44	1.39	3.06	160	139	357	48	15	27	31	130	36	38
Mo 4 (1)S 1970	0-10	2.82	2.93	6.08	0.70	57.20	13.03	1.78	0.29	0.08	1.66	3.12	0.07	3.09	101	245	367	51	17	78	23	115	23	60
	10-20	2.68	2.91	5.31	0.66	55.31	12.82	1.53	0.27	0.08	2.10	5.25	0.15	5.20	101	249	339	45	14	43	15	76	20	46
	20-30	2.66	3.02	5.09	0.68	56.34	13.12	1.45	0.27	0.07	1.77	5.30	0.15	5.26	102	230	336	42	15	35	14	76	20	58
	30-40	2.66	3.07	5.13	0.70	56.79	12.50	1.73	0.23	0.08	1.90	4.88	0.11	4.85	109	242	331	47	21	27	15	78	23	46
	40-50	2.73	3.08	4.95	0.64	58.45	12.89	1.62	0.23	0.07	1.37	4.11	0.07	4.09	92	233	294	35	13	17	15	69	20	42
	50-60	2.80	3.22	5.13	0.68	59.74	13.46	1.48	0.23	0.08	1.52	3.52	0.04	3.51	112	281	366	51	17	21	17	73	22	45
	60-70	2.74	3.22	5.51	0.69	58.86	13.37	1.72	0.23	0.07	1.65	3.08	0.07	3.06	105	259	350	49	18	31	17	74	21	57
	70-80	2.77	3.20	4.70	0.63	59.48	12.97	1.40	0.19	0.07	1.35	2.16	0.11	2.13	112	286	364	44	19	21	14	72	20	47

Table D.3 continued

Station and Date	Depth (cm)	Major elements (in wt.%)													Trace elements (in ppm)								
		CaO	K_2O	Fe_2O_3	TiO_2	SiO_2	Al_2O_3	MgO	P_2O_5	MnO	S	Total C	CO_2	Organic C	Rb	Zr	Sr	Y	Nb	Pb	Cu	Zn	Ni	Mo
Mo 7 (2)S	0-10	3.42	2.43	6.94	0.68	47.37	10.49	1.65	0.28	0.12	2.98	7.43	0.00	7.43	90	158	339	46	12	83	27	131	26	59
1970	10-20	3.22	2.78	6.09	0.96	53.05	12.02	2.03	0.35	0.08	1.91	5.54	0.12	5.51	101	213	420	41	15	42	19	97	27	51
	20-30	3.13	2.62	6.29	0.83	51.17	11.73	2.15	0.29	0.10	2.40	5.62	0.12	5.59	97	222	387	50	18	32	23	95	27	67
	30-40	3.42	2.61	6.01	0.70	50.67	11.01	1.43	0.23	0.10	2.14	5.64	0.00	5.64	110	185	352	41	20	31	25	100	26	56
	40-50	3.11	3.12	6.14	0.71	54.60	12.38	1.89	0.29	0.10	2.03	4.73	0.04	4.72	123	217	356	52	16	28	22	99	27	55
	50-60	3.18	2.95	6.70	0.92	54.89	12.86	2.31	0.34	0.11	1.93	3.19	0.11	3.16	113	222	422	42	19	32	21	98	30	55
	60-70	3.22	3.00	5.87	0.82	54.73	12.20	1.96	0.30	0.09	2.12	4.67	0.15	4.63	115	238	405	49	13	22	16	91	26	55
	70-80	3.00	3.31	6.07	0.78	58.79	13.63	2.09	0.30	0.09	1.30	1.99	0.04	1.98	130	237	385	47	18	29	23	102	27	56
	80-90	3.24	3.13	5.63	0.75	56.78	13.26	1.86	0.28	0.08	1.89	3.47	0.11	3.44	112	209	385	48	15	31	22	94	26	60
	90-100	3.01	3.27	5.92	0.79	56.73	12.96	2.12	0.27	0.09	1.96	3.11	0.11	3.08	117	182	356	37	15	17	19	94	26	48
	100-110	3.13	3.00	6.53	0.80	54.86	13.06	2.23	0.27	0.11	2.05	3.78	0.11	3.75	111	192	369	48	15	21	20	100	28	63
	110-130	3.55	2.89	6.33	0.71	53.04	12.42	1.77	0.29	0.15	2.59	5.56	0.19	5.51	111	189	359	48	16	21	26	104	30	59
Mo 26	0- 5	7.89	2.03	5.35	0.58	44.68	9.77	1.12	0.26	0.02	0.97	9.90	4.62	8.64	83	152	410	37	12	88	30	139	29	26
1970	5-10	5.75	2.50	3.94	0.60	57.35	11.05	0.84	0.23	0.03	0.67	6.56	2.47	5.89	92	264	377	40	14	34	15	65	22	18
	10-15	9.21	2.07	5.11	0.56	45.31	10.12	1.03	0.26	0.03	1.07	8.22	4.96	6.86	81	149	466	32	16	40	23	91	26	32
	15-20	8.77	2.39	4.28	0.61	57.00	11.30	0.56	0.24	0.03	1.14	7.90	4.94	6.55	82	144	492	39	14	28	27	102	28	29
	20-25	8.70	2.31	4.19	0.55	46.64	9.68	1.14	0.20	0.03	1.09	7.11	4.57	5.87	88	196	456	45	13	24	22	81	27	28
	25-30	8.41	2.38	4.11	0.53	46.98	9.72	1.21	0.21	0.03	1.01	6.42	4.37	5.23	93	194	458	42	12	31	22	78	24	21
	30-35	6.71	2.52	4.38	0.56	53.65	11.04	1.30	0.20	0.03	1.07	5.37	3.07	4.54	98	226	415	40	18	23	18	73	24	25
	35-40	7.67	2.60	4.48	0.59	48.43	10.52	1.25	0.25	0.04	1.16	6.51	3.91	5.44	107	184	416	40	15	21	23	87	27	29
	40-45	8.75	2.39	6.81	0.49	42.74	9.64	1.24	0.24	0.03	1.42	6.75	4.91	5.42	96	175	468	42	13	20	22	89	30	32
	45-50	9.50	2.37	4.74	0.52	39.93	9.27	1.33	0.23	0.04	1.54	8.49	5.93	6.87	104	142	474	40	17	25	27	105	32	31
	50-55	8.56	3.00	4.97	0.62	49.98	11.42	1.51	0.24	0.05	1.28	5.56	4.61	4.30	117	157	465	40	17	23	24	99	29	24
	55-60	9.10	2.79	4.81	0.58	47.58	11.11	1.66	0.27	0.05	1.20	5.48	4.88	4.15	113	171	483	41	17	18	25	107	28	24
	60-65	10.15	2.79	4.71	0.56	48.21	10.83	1.55	0.22	0.04	0.94	5.15	5.87	3.55	108	176	519	38	17	20	22	83	26	23
	65-70	12.11	2.51	3.57	0.48	51.10	10.67	0.87	0.24	0.03	0.97	4.15	7.68	2.05	92	227	629	36	11	15	13	50	19	22
	70-75	14.29	2.24	4.13	0.45	44.69	9.12	0.68	0.21	0.03	1.45	6.68	9.24	4.16	78	190	626	35	14	17	18	67	23	32
Mo 8	0- 5	4.81	2.31	4.72	0.62	46.31	10.32	1.69	0.22	0.05	1.26	9.07	1.45	8.67	94	149	327	42	12	66	25	120	28	31
1970	5-10	5.54	2.26	4.77	0.56	43.87	9.65	1.60	0.23	0.05	1.81	9.21	1.80	8.72	96	148	319	47	14	42	25	109	29	49
	10-15	4.37	2.59	7.50	0.63	48.52	10.94	1.54	0.24	0.06	1.66	7.04	1.31	6.68	105	179	332	43	14	31	28	102	30	55
	15-20	6.04	2.21	4.07	0.51	46.70	10.02	1.56	0.23	0.06	1.80	7.84	1.32	7.48	104	141	318	42	17	27	27	111	28	56
	20-25	6.77	2.34	4.43	0.50	48.96	9.79	1.21	0.19	0.06	1.67	7.30	0.78	7.08	100	159	325	48	14	21	24	99	26	63
	25-30	7.46	2.54	3.89	0.54	55.35	10.64	1.06	0.19	0.03	1.02	4.47	3.48	3.52	90	223	432	41	13	14	12	64	19	49
	30-35	8.11	2.58	3.48	0.49	54.55	10.60	1.00	0.17	0.04	0.85	4.27	4.75	2.98	92	204	453	40	17	17	13	56	16	50
	35-40	3.82	2.76	5.20	0.60	52.05	11.62	1.63	0.22	0.07	1.65	5.88	1.45	5.49	104	174	333	42	14	19	22	89	24	54
	40-45	5.03	2.47	4.58	0.57	49.49	10.60	1.42	0.21	0.05	1.52	6.76	2.04	6.20	97	180	343	48	14	23	22	97	26	38
	45-50	4.85	3.20	5.09	0.65	53.15	12.42	1.77	0.23	0.07	1.31	4.94	1.59	4.50	127	178	362	48	16	28	24	109	28	30
	50-55	8.23	2.76	4.36	0.55	49.52	10.63	1.28	0.19	0.05	1.25	6.12	3.77	5.09	104	200	450	42	16	21	19	86	23	43
	55-57.5	11.21	2.61	3.13	0.46	52.65	10.18	0.91	0.17	0.03	0.57	3.74	7.23	1.77	90	228	571	41	14	24	12	49	16	24
Mo 34	0- 3	9.14	2.54	5.56	0.54	46.68	10.48	1.61	0.28	0.06	2.18	6.67	4.30	5.50	81	136	382	38	6	59	31	159	34	94
1970	3- 6	10.60	2.87	4.98	0.54	48.38	10.78	1.65	0.24	0.05	1.57	5.89	6.08	4.23	102	193	602	39	8	28	17	105	23	53
	6- 8	12.64	2.24	5.30	0.53	43.67	10.07	1.75	0.27	0.06	2.16	7.87	6.20	6.18	80	139	550	29	9	18	24	85	34	81

Table D.3 continued

Station and Date	Depth (cm)	Major elements (in wt.%)													Trace elements (in ppm)									
		CaO	K_2O	Fe_2O_3	TiO_2	SiO_2	Al_2O_3	MgO	P_2O_5	MnO	S	Total C	CO_2	Organic C	Rb	Zr	Sr	Y	Nb	Pb	Cu	Zn	Ni	Mo
Mo 49	0- 4	3.07	2.44	5.91	0.64	48.65	11.24	1.70	0.29	0.09	2.28	3.70	0.12	8.89	91	176	300	41	11	72	20	129	26	59
1971	4- 7	2.84	2.44	6.18	0.64	50.61	11.60	1.85	0.27	0.09	2.38	3.90	0.12	5.86	93	178	309	39	12	61	15	99	25	56
	7-10	2.68	2.54	5.18	0.70	55.37	12.54	1.85	0.29	0.06	1.61	5.05	0.00	5.21	85	217	338	40	16	37	12	76	22	51
Mo 14	0- 5	5.92	2.34	4.79	0.61	49.18	11.17	1.37	0.29	0.04	0.74	8.78	3.09	7.94	90	153	346	40	16	129	33	174	26	29
1970	5-10	4.95	2.14	4.74	0.61	45.01	10.46	1.58	0.25	0.03	0.95	9.35	2.82	8.58	85	169	355	41	16	89	30	146	25	33
	10-15	5.37	1.75	3.55	0.46	32.72	7.12	2.44	0.22	0.05	1.70	9.95	2.36	9.30	86	152	339	46	14	55	25	122	29	55
	15-20	5.64	2.31	4.51	0.55	47.57	10.06	1.38	0.28	0.04	1.31	8.67	2.35	8.03	88	158	343	42	15	40	22	105	25	51
	20-25	6.41	2.32	4.85	0.58	46.90	10.40	1.46	0.28	0.05	1.80	10.00	2.51	9.32	86	133	332	43	13	38	23	113	27	57
	25-30	5.02	2.28	4.33	0.51	38.93	8.92	1.94	0.21	0.06	1.72	7.92	1.84	7.41	108	170	323	50	16	36	25	111	27	68
	30-35	5.14	2.18	4.24	0.49	38.28	8.50	2.31	0.21	0.06	1.75	8.28	1.80	7.78	101	157	335	43	18	30	21	107	26	64
	35-40	5.11	2.62	4.36	0.58	53.15	11.37	1.45	0.26	0.04	1.37	7.05	2.13	6.47	88	145	296	33	13	18	20	96	24	44
	40-45	5.26	2.61	4.56	0.57	52.34	11.37	1.30	0.27	0.04	1.59	7.10	2.01	6.55	103	172	342	39	12	16	19	91	22	72
	45-50	8.31	2.74	3.55	0.52	56.06	10.93	0.83	0.15	0.04	0.99	4.25	4.62	2.99	94	184	454	37	14	15	17	58	18	40
Mo 10	0- 5	2.74	2.77	5.40	0.72	62.25	14.65	1.16	0.34	0.05	0.51	5.87	0.13	5.83	102	259	333	38	17	49	18	76	26	30
1970	5-10	2.78	2.79	3.99	0.65	59.90	12.88	1.44	0.24	0.04	0.50	4.09	0.04	4.08	101	314	359	39	19	39	15	67	20	20
	10-15	2.65	2.94	3.71	0.62	62.76	13.40	1.27	0.24	0.04	0.30	3.32	0.07	3.30	99	301	357	37	14	49	13	75	20	12
	15-20	2.72	2.65	3.85	0.63	58.78	12.88	1.31	0.21	0.04	0.57	4.75	0.04	4.74	95	317	362	44	14	58	14	77	20	16
	20-25	2.74	2.76	3.85	0.65	60.67	12.93	1.41	0.21	0.04	0.52	4.01	0.07	3.99	100	368	360	38	17	38	14	58	19	16
	25-30	2.73	2.80	3.83	0.61	63.76	13.03	1.46	0.20	0.04	0.63	2.53	0.12	2.50	98	331	373	40	16	30	12	50	18	16
	30-35	2.73	2.83	3.88	0.63	62.82	12.84	1.24	0.24	0.04	0.72	2.99	0.15	2.95	99	363	368	42	18	28	7	45	18	29
	35-41.5	2.70	2.74	3.79	0.60	64.05	13.08	1.29	0.25	0.04	0.62	2.66	0.07	2.64	91	338	371	40	16	29	8	41	16	27
Bo 1	0- 1.5	2.25	2.42	7.66	0.84	48.70	13.69	2.48	0.41	0.10	1.61	7.04	0.08	7.01	98	185	253	42	11	78	36	146	38	32
1971	1.5- 3.5	2.34	2.71	7.25	0.87	50.20	14.52	2.42	0.40	0.10	1.52	7.81	0.15	7.77	107	202	280	46	12	58	30	117	37	24
	3.5- 5.5	2.42	2.59	6.77	0.85	50.30	14.55	2.60	0.36	0.09	1.33	6.27	0.00	6.27	103	208	289	45	11	42	26	108	35	19
	5.5- 9	2.55	2.60	5.78	0.85	56.14	14.05	2.02	0.34	0.08	1.01	4.06	0.08	4.04	100	223	351	38	14	34	14	83	27	15
	9-15	2.34	2.43	7.15	0.79	47.73	13.75	2.41	0.37	0.12	1.82	8.09	0.08	8.07	94	193	275	41	14	37	33	101	36	28
	15-20	2.53	2.70	6.80	0.69	52.77	14.33	2.34	0.34	0.10	1.38	4.30	0.00	4.30	105	230	307	47	15	30	23	87	33	18
	20-22	2.96	2.37	5.47	0.90	64.01	13.49	2.15	0.22	0.08	0.50	1.02	0.15	0.98	87	269	275	44	15	22	22	68	31	1
	22-30	2.58	2.55	6.68	0.85	52.84	14.24	2.58	0.37	0.09	1.47	4.93	0.07	4.91	94	208	266	44	14	30	22	83	33	14
	30-40.5	2.63	2.67	6.85	0.87	56.52	14.49	2.48	0.34	0.09	1.33	3.35	0.11	3.32	106	235	279	45	11	29	23	95	33	14
	40.5-45	2.68	3.19	6.85	0.86	58.33	16.11	2.90	0.27	0.09	0.51	1.00	0.22	0.94	126	229	258	44	16	26	19	94	42	7
	45-53.5	2.54	3.60	6.97	0.93	58.58	16.71	2.89	0.24	0.09	0.34	0.49	0.07	0.46	138	234	245	49	15	20	14	104	40	2
	53.5-60	2.69	2.64	7.36	0.85	55.02	13.54	2.52	0.37	0.11	1.47	4.00	0.04	3.99	94	220	274	44	11	13	19	88	32	26
	60-71	2.73	2.64	7.08	0.87	54.61	14.80	2.42	0.35	0.11	1.69	4.54	0.15	4.50	101	219	293	45	12	25	22	86	31	28
	71-81	2.80	2.77	6.74	0.88	57.87	14.85	2.27	0.38	0.13	1.31	3.50	0.15	3.46	104	236	319	48	10	26	23	92	35	21
	81-90	2.68	2.58	6.61	0.85	56.60	14.20	2.57	0.35	0.16	1.41	3.09	0.15	3.05	94	240	280	41	14	23	22	90	34	19
	90-93	3.01	2.42	5.41	0.86	65.28	13.96	2.17	0.26	0.09	0.38	0.44	0.22	0.38	87	259	276	46	13	16	15	64	26	3
	93-100	2.50	2.55	7.68	0.86	52.54	14.21	2.49	0.36	0.14	2.13	5.07	0.15	5.03	99	208	289	45	10	21	30	100	34	31
	100-105	2.56	2.42	5.43	0.78	55.94	13.82	1.95	0.40	0.08	1.36	4.99	0.04	4.98	85	214	332	41	9	29	7	71	25	19
	105-106	2.24	2.61	3.36	0.54	67.19	13.55	0.86	0.20	0.06	0.57	1.17	0.04	1.16	89	164	398	27	11	33	11	41	15	10
	106-120	2.65	2.52	6.50	0.89	57.36	14.02	2.15	0.34	0.10	1.52	3.46	0.15	3.42	100	238	311	39	12	21	20	83	32	24

Table D.3 continued

Station and Date	Depth (cm)	Major elements (in wt.%)													Trace elements (in ppm)								
		CaO	K_2O	Fe_2O_3	TiO_2	SiO_2	Al_2O_3	MgO	P_2O_5	MnO	S	Total C	CO_2	Organic C	Rb	Zr	Sr	Y	Nb	Pb	Cu	Zn	Ni	Mo
Bo 6 1971	0- 2	2.56	2.27	7.59	0.76	46.47	13.69	2.51	0.45	1.34	1.39	7.16	0.85	6.93	99	190	292	43	15	69	33	172	42	43
	2- 4	2.48	2.48	7.33	0.78	47.78	13.57	2.41	0.43	0.63	1.62	6.66	0.48	6.52	100	197	286	44	12	81	32	166	34	45
	4- 6	2.40	2.55	8.18	0.81	47.86	13.88	2.32	0.47	0.56	2.00	7.06	0.56	6.91	97	189	305	47	12	78	30	144	36	47
	6- 8	2.69	2.65	6.95	0.80	48.62	13.80	2.33	0.38	0.81	1.43	5.35	0.40	5.24	102	205	349	43	15	66	29	123	36	35
	8-10	2.92	2.82	5.70	0.85	58.06	14.52	2.08	0.27	0.18	0.58	3.03	0.11	3.00	107	239	442	40	18	37	10	77	33	13
	10-17	2.64	2.71	7.71	0.87	48.42	14.01	2.52	0.48	0.53	1.69	6.62	0.31	6.53	104	198	366	42	16	49	28	107	37	29
	17-23	2.59	3.01	7.68	0.86	50.53	15.23	2.68	0.41	0.49	1.22	4.74	0.31	4.66	115	205	321	47	16	40	30	108	41	25
	23-35	2.88	2.80	8.47	0.79	46.23	14.26	2.82	0.42	1.59	2.09	6.22	1.16	5.90	115	180	327	45	13	36	26	99	40	36
	35-38	2.16	3.80	8.34	0.86	52.35	17.21	3.16	0.27	0.38	0.79	2.38	0.34	2.29	155	211	264	46	11	22	20	119	47	20
	38-51	2.87	2.82	9.09	0.78	46.10	14.34	2.68	0.41	1.93	2.48	5.18	1.27	4.84	111	184	309	43	12	19	24	106	36	47
	51-57	2.61	2.86	5.57	0.70	53.41	13.37	1.99	0.29	0.23	1.31	6.90	0.15	6.86	97	171	391	41	12	28	9	71	27	20
	57-65	2.47	2.93	6.22	0.72	53.92	13.72	2.15	0.32	0.24	1.49	5.70	0.15	5.66	99	169	340	39	11	28	13	81	31	26
	65-71	2.58	2.73	7.94	0.76	49.29	13.77	2.37	0.40	0.67	2.16	6.30	0.34	6.21	101	163	322	40	14	28	25	100	39	34
	71-74	2.54	3.11	6.96	0.70	54.41	14.92	2.45	0.34	0.30	1.46	3.98	0.00	3.98	116	173	334	44	12	22	19	87	32	24
	74-80	2.55	2.99	7.18	0.77	55.16	14.56	2.19	0.32	0.26	1.58	4.07	0.23	4.01	101	186	327	39	10	29	22	89	34	24
	80-86	2.40	3.49	4.38	0.60	66.51	14.60	1.57	0.22	0.11	0.50	0.88	0.04	0.87	120	180	421	31	12	21	6	67	29	9
	86-98	2.66	2.97	8.50	0.72	49.47	14.69	2.79	0.35	1.03	2.43	4.93	0.80	4.72	117	188	323	46	16	29	21	112	41	32
	98-103	2.52	2.79	8.30	0.79	49.73	13.94	2.05	0.33	0.31	2.41	5.78	0.26	5.70	103	188	317	45	12	32	28	106	35	32
Bo 2A 1971	0- 2	2.26	2.48	8.30	0.74	42.40	12.85	2.33	0.41	0.57	2.84	7.07	0.19	7.01	94	180	278	41	12	79	27	152	32	48
	2- 5	2.64	2.77	6.98	0.83	48.57	14.11	2.03	0.36	0.70	1.45	5.42	0.26	5.35	109	229	352	44	12	43	25	113	38	30
	5- 7	2.55	2.74	7.22	0.85	50.74	14.96	2.62	0.38	0.29	1.49	4.68	0.26	4.61	113	213	331	44	12	47	25	113	33	23
	7-10	2.29	2.57	7.98	0.80	44.26	13.65	2.66	0.44	0.26	2.35	8.01	0.04	8.00	102	177	275	40	11	56	26	119	33	45
	10-15	3.81	3.04	8.38	1.17	49.97	14.89	4.46	0.66	0.42	1.89	6.95	0.27	6.87	108	196	331	42	14	39	30	104	38	22
	15-20	2.37	2.57	7.92	0.85	45.06	13.61	2.38	0.44	0.44	2.32	7.73	0.08	7.71	97	194	313	41	13	45	20	97	34	36
	20-24.5	2.40	2.87	7.90	0.86	47.22	14.91	2.88	0.41	0.44	1.61	5.76	0.34	5.67	104	191	286	45	9	40	32	99	41	40
	24.5-26.5	2.86	3.10	6.84	0.84	57.37	15.68	2.76	0.33	0.12	0.61	1.77	0.15	1.73	120	244	313	48	14	28	33	97	40	8
	26.5-35	2.52	2.74	8.08	0.83	47.66	14.24	2.14	0.44	0.45	1.99	5.84	0.15	5.80	104	189	290	44	10	34	25	107	43	22
	35-44.5	2.36	3.04	8.80	0.80	48.73	14.98	2.76	0.36	0.46	2.01	4.82	0.42	4.71	120	209	299	48	13	25	22	120	38	22
	44.5-46	2.02	4.10	8.35	0.88	53.63	18.12	3.48	0.26	0.20	0.61	0.95	0.00	0.95	169	209	217	49	19	24	23	114	45	9
	46-56	2.45	2.80	9.42	0.80	46.94	14.71	2.76	0.39	0.64	2.56	4.94	0.26	4.87	101	184	279	50	10	19	26	111	37	41
	56-63.5	2.59	2.71	9.10	0.75	45.11	13.75	2.44	0.40	1.38	2.77	5.64	0.54	5.49	106	177	298	44	11	27	26	105	42	54
	63.5-65.5	2.52	3.50	7.66	0.84	54.33	16.30	2.73	0.29	0.52	0.90	1.89	0.04	1.88	145	208	293	42	14	30	26	111	45	15
	65.5-75	2.49	2.72	7.64	0.81	51.05	14.66	2.43	0.38	0.29	1.98	4.56	0.00	4.56	105	212	324	44	16	26	24	107	32	37
	75-85	2.54	2.82	7.32	0.86	51.02	14.42	2.41	0.50	0.26	1.83	4.63	0.12	4.60	102	246	391	43	13	23	19	97	34	29
Bo 2 1971	0-21	2.59	2.67	6.67	0.83	52.54	14.68	2.25	0.37	0.11	1.36	5.10	0.04	5.09	107	254	387	50	14	51	35	112	32	16
	21-24	2.52	2.84	6.81	0.81	54.27	14.61	2.66	0.35	0.10	1.11	3.16	0.11	3.13	121	236	298	51	16	24	28	89	37	10
	24-33.5	2.35	2.75	7.66	0.85	48.04	14.62	2.09	0.40	0.16	2.06	6.14	0.12	6.11	119	218	309	49	17	34	31	95	36	22
	33.5-39.5	2.12	3.98	8.28	0.91	52.49	17.59	2.24	0.23	0.13	0.64	0.98	0.07	0.96	170	217	248	46	16	23	36	119	48	6
	39.5-49.5	2.91	2.48	5.76	0.82	59.15	13.72	2.12	0.32	0.22	1.01	2.74	0.11	2.71	100	292	432	47	15	27	23	81	28	8
	49.5-63	2.55	2.87	7.45	0.83	53.02	14.88	2.52	0.41	0.14	1.61	3.70	0.11	3.67	115	246	373	53	17	20	30	98	32	23
	63-70	2.53	2.81	7.94	0.82	48.05	13.92	2.32	0.40	0.59	2.10	3.90	0.07	3.88	108	217	330	53	13	33	29	105	36	20
	70-83	2.37	2.82	8.19	0.85	49.71	14.54	2.53	0.43	0.27	2.31	5.05	0.04	5.04	121	223	348	43	15	24	33	101	37	32

Table D.3 continued

Station and Date	Depth (cm)	Major elements (in wt.%)												Trace elements (in ppm)								
		CaO	K_2O	Fe_2O_3	TiO_2	SiO_2	Al_2O_3	MgO	P_2O_5	MnO	S	Total C	CO_2	Organic C	Rb	Zr	Sr	Y	Nb	Pb	Cu	Zn	Ni	Mo
Bo 1A 1971	0-10	2.40	2.66	6.67	0.86	50.14	14.26	2.50	0.43	0.09	1.73	6.06	0.04	6.05	116	234	357	48	14	43	32	106	35	16
	10-20	2.37	2.59	6.98	0.80	48.97	13.97	2.38	0.39	0.10	1.85	6.85	0.04	6.84	103	211	299	47	19	39	30	95	34	21
	20-27	2.56	2.64	6.43	0.90	53.51	13.94	1.98	0.33	0.09	1.23	3.89	0.07	3.87	107	248	343	50	13	31	30	84	35	3
	27-34	2.54	2.53	6.47	0.88	53.41	13.97	2.30	0.37	0.08	1.50	4.19	0.04	4.18	101	238	307	50	11	24	30	84	33	11
	34-39	2.53	2.78	6.82	0.83	54.23	14.71	2.40	0.35	0.09	1.76	3.32	0.11	3.29	113	229	282	33	11	29	31	92	39	20
	39-46	2.55	3.27	6.93	0.90	57.15	16.14	2.81	0.28	0.09	0.79	1.36	0.07	1.34	131	258	268	56	19	20	29	93	41	5
	46-52	2.45	2.80	6.84	0.84	53.35	14.42	2.49	0.31	0.11	1.50	3.66	0.04	3.65	115	239	280	53	16	22	26	87	34	18
	52-58	2.44	2.68	7.27	0.84	51.75	14.16	2.64	0.39	0.10	1.94	4.75	0.11	4.72	109	229	314	42	13	26	31	93	34	24
	58-64	2.68	2.67	6.64	0.89	53.56	13.87	2.35	0.39	0.10	1.51	4.34	0.04	4.33	108	248	383	56	14	25	29	91	31	13
	64-71	2.53	2.64	6.89	0.87	53.23	14.66	2.39	0.37	0.12	1.75	4.05	0.11	4.02	108	246	329	49	15	26	31	92	35	22
	71-76	2.56	2.63	6.80	0.84	54.59	14.08	2.48	0.36	0.11	1.70	3.48	0.11	3.45	115	236	304	46	15	22	28	90	36	24
	76-82	2.63	2.63	6.55	0.87	57.61	14.27	2.45	0.32	0.12	1.34	2.41	0.04	2.40	114	268	304	52	18	24	32	81	34	14

TABLE D.4

Correlation matrix for sediment data

number of samples = 174

correlation coefficients > 0.20 are significant at 0.05 confidence level

	CaO	K_2O	Fe_2C_3	TiO_2	SiO_2	Al_2O_3	P_2O_5	MgO	MnO	S	CO_2	Org C	Sr	Zn	Cu	U	Pb	Mo	Ni	Rb	Nb	Zr
K_2O	-0.08																					
Fe_2C_3	-0.43	0.23																				
TiO_2	-0.45	0.26	0.50																			
SiO_2	-0.11	0.34	-0.18	0.18																		
Al_2O_3	-0.49	0.43	0.49	0.62	0.26																	
P_2C_5	-0.46	0.00	0.58	0.49	-0.13	0.40																
MgO	-0.38	0.29	0.65	0.56	-0.02	0.58	0.48															
MnO	-0.48	0.23	0.69	0.45	-0.08	0.48	0.54	0.59														
S	-0.15	-0.25	0.21	-0.01	-0.34	-0.12	0.28	0.04	0.22													
CO_2	0.63	-0.10	-0.20	-0.38	-0.30	-0.33	-0.28	-0.22	-0.28	-0.10												
Org C	0.01	-0.51	-0.02	-0.23	-0.52	-0.33	0.15	-0.16	-0.05	0.45	0.11											
Sr	0.50	-0.00	-0.39	-0.36	0.03	-0.35	-0.32	-0.41	-0.35	-0.13	0.35	-0.07										
Zn	0.03	0.14	0.34	0.10	-0.32	0.09	0.17	0.30	0.24	0.05	0.18	0.13	-0.11									
Cu	-0.09	-0.04	0.38	0.21	-0.34	0.13	0.29	0.31	0.28	0.15	0.04	0.18	-0.19	0.46								
U	0.17	-0.27	-0.16	-0.29	-0.21	-0.33	-0.12	-0.21	-0.14	0.21	0.17	0.29	0.09	-0.03	-0.13							
Pb	-0.10	-0.06	0.09	0.04	-0.12	-0.00	0.16	0.04	0.09	-0.04	-0.06	0.21	-0.07	0.34	0.17	-0.03						
Mo	0.17	-0.28	-0.08	-0.32	-0.32	-0.41	-0.03	-0.21	-0.06	0.53	0.13	0.46	0.10	0.02	0.01	0.33	-0.05					
Ni	-0.29	0.20	0.67	0.44	-0.18	0.45	0.45	0.63	0.57	0.08	-0.08	-0.05	-0.34	0.39	0.52	-0.17	0.07	-0.19				
Rb	-0.11	0.67	0.30	0.32	0.17	0.43	0.07	0.39	0.28	-0.18	-0.09	-0.40	-0.07	0.29	0.17	-0.25	-0.04	-0.30	0.35			
Nb	0.11	0.22	-0.12	0.01	0.21	0.01	-0.18	-0.03	-0.13	-0.22	-0.05	-0.21	0.15	-0.01	-0.06	-0.12	-0.03	-0.09	-0.11	0.27		
Zr	-0.30	0.11	-0.00	0.32	0.46	0.26	0.11	0.06	0.05	-0.10	-0.43	-0.29	-0.10	-0.38	-0.20	-0.20	-0.06	-0.24	-0.07	0.04	0.14	
Y	-0.23	0.17	0.25	0.33	0.05	0.26	0.18	0.29	0.24	0.07	-0.25	-0.11	-0.22	0.12	0.21	-0.19	-0.02	-0.10	0.23	0.31	0.16	0.22

APPENDIX E

Description of Sediment Cores

The sediment cores were logged immediately after being cut longitudinally into two sections (p. 98). Thus no description exists of the cores used for interstitial water sampling.

Basin	Core	Water depth[1] (m)	Core length (cm)	Description
Inner Mofjord	Mo 8	163	57.5	Brown, sandy clay with significant amounts of terrestrial plant debris and fragmented/whole bivalves.
Inner Mofjord	Mo 10	69	41.5	Dark brown, sandy silt containing terrestrial plant debris, including twigs.
Inner Mofjord	Mo 14	163	50	Brown, sandy clay with terrestrial plant debris and fragmented/whole bivalves.
Inner Mofjord	Mo 49	213	33	Dark brown to black silty clay; organic-rich with abundant leaf material; irregular grey laminations; coarser (grit) horizons at 21-25cm containing twigs.
Outer Mofjord	Mo 26	78	75	Brown, sandy clayey silt; abundant shell material (fragmented/whole bivalves); some coarse (sand) horizons with twigs; generally organic-rich and containing numerous polychaete dwelling tubes.

1 Measured with metre-wheel

Basin	Core	Water depth (m)	Core length (cm)	Description
Holvikefjord	No 34	231	105	0-~45cm: dark brown, organic-rich, silty clay with abundant leaves; irregularly distributed complete and fragmented bivalves; irregular grey laminations. ~45-105cm: homogeneous olive-green clay.
Osterfjord	No 22	240	14	Light blue-grey clay with some bivalve fragments.
Osterfjord	No 23	220	22	Dark green-grey silty clay containing small bivalve fragments and a few leaves and twigs.
Osterfjord	No 42	243	10	Light blue-grey clay with a few bivalve fragments.
Osterfjord	No 44	462	21	Blue-grey silty clay with reddish-brown coloured, surface layer (~1cm); contains some shell fragments.
Osterfjord	No 45	455	10	Light blue-grey clay with reddish-brown coloured, surface layer (~1cm); some shell fragments included.
Bolstadfjord	No 1	88	123	Dark brown to black silty clay; organic-rich with abundant leaf material and twigs; some irregular grey laminations and thicker bands of grey silt or coarse (grit) material, the latter including numerous twigs.

Basin	Core	Water depth (m)	Core length (cm)	Description
Bolstadfjord	Bo 2A	131	114	Dark brown, organic-rich silty clay; abundant leaf material; some irregular grey coloured laminations and thicker horizons of grey clay or silt.
Bolstadfjord	Bo 6	147	104	Dark brown to black, organic-rich silty clay; containing many leaves and irregular grey coloured laminations; some grey silt bands and coarse grained (grit) horizons with numerous twigs.

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